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AGGREGATION OF COBALT (II) TETRASULFONATED PHTHALOCYANINE IN METHANOL-WATER SOLUTIONS

by

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Chemical Branch
Research Division

June 1983

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Metal complexes of tetrasulfonated phthalocyanine (TSPC) are of interest as oxidation and hydrolysis catalysts for thioethers and organophosphonates. Since metal TSPC complexes aggregate in aqueous solution, it was necessary to determine the dimerization constant as a prerequisite to establishing the efficiency of the monomeric TSPC complexes as catalysts. Since these complexes will be used in mixed solvents to dissolve thioethers, the aggregation of the Cobalt (II) TSPC (CoTSPC) was measured in methanol-water
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20. ABSTRACT (Cont'd)

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solutions at various temperatures. The dimerization constant was determined by a nonlinear least-squares fit of absorbance versus concentration of CoTSPC. Values of the molar absorption coefficients for the monomer and dimer at 662 nm are 9.6 $\pm 10^5$/M and 7.5 ± 0.8 x 10^5 M^{-2}/cm^{-2}, respectively, with the error representing the standard deviation of four solutions measured at five-degree intervals over the range 15-45° C.

(Delta) *(Δ)*

The dimerization of CoTSPC in the presence of methanol was measured over the same temperature range with methanol percent mole fraction from 0.4 to 9.8. The temperature dependence of the free energy of dimerization in methanol-water was expressed as $\Delta F^\circ = A + BT + CT^2$ indicating that the heat capacity of dimerization was linearly dependent on temperature. In pure water the heat capacity of dimerization was zero.

PREFACE

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AGGREGATION OF COBALT (II) TETRASULFONATED PHTHALOCYANINE IN METHANOL-WATER SOLUTIONS

1. INTRODUCTION

In 1971 Abel and coworkers[1] discovered that the cobalt (II) tetra-sulfonated phthalocyanine (TSPC), figure 1, binds oxygen reversibly as do oth'r cobalt (II) complexes with Schiff bases, prophyrins, corrin, or dimetnvigloxime.[2,3] Abel's discovery led to further work with oxygenated metal iSPC complexes[4-11] and helped to stimulate work with metal TSPC complexes as mimics of biological oxygen carriers[12-17] as well as oxidation catalysts in homogeneous solution [18-23] and on various supports.[24-34]
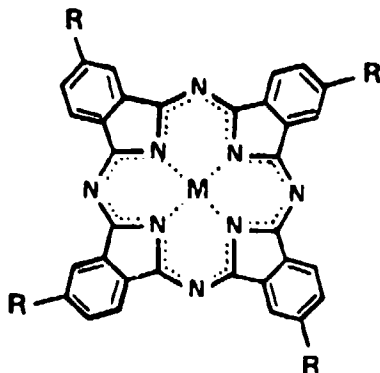
$$R = SO_3Na \ (TSPC)$$

$$M = Co^{++}; \ Cu^{++}$$

Figure 1. Structure of Metal Phthalocyanines

Metal TSPC complexes aggregate in aqueous solution[35-56] in concert with other dyestuffs[57] which means that equilibrium constants for aggregation are needed to determine conditions in which the particular species exist in solutions of such complexes. We are interested in whether metal TSPC complexes, particularly cobalt (II) TSPC (CoTSPC), catalyze reactions of oxygen with thioethers and organophosphonates in mixed solvents containing water as one component. The organic cosolvent is necessary to increase the solubility of the hydrophobic thioethers. Thus, experiments are required to determine equilibrium constants for aggregation of the metal TSPC complexes in such mixed solvents.

Abel and his coworkers measured dimerization constants of CoTSPC in a series of methanol-water and ethanol-water solutions ranging from pure water to 50 percent by volume of alcohol. These measurements were restricted to a single temperature (20° C), so no enthalpy or entropy values of dimerization are available.[52] By contrast, Blagrove and Gruen[47] measured these thermodynamic parameters for the dimerization of CoTSPC, but their measurements were restricted to a single alcohol-water mixture (20 percent by volume of methanol or ethanol).

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This report begins to bridge the gap between these two extremes by measuring the enthalpy and entropy of dimerization for CoTSPC in a series of methanol-water mixtures over a range of temperatures.

2. MATERIAL AND METHODS

2.1 Preparation of [29H,31H-phthalocyanine-2,9,16,23-tetrasulfonate(2-)-N²⁹,N³⁰,N³¹,N³²] Cobalt (CoTSPC).

This material was prepared by the method of Weber and Busch[58] using the sodium salt of 4-sulfophthalic acid, ammonium chloride, urea, ammonium molybdate, and cobalt sulfate heptahydrate in hot nitrobenzene. The purification procedure for this 0.05-mole scale reaction differed slightly from the published method. The crude, dark-blue product was broken apart with a spatula, rinsed with 400 ml methanol, and was finely ground in a mortar. The resulting blue powder was dissolved in 1.1 liters of 1N HCl saturated with sodium chloride to give a deep blue slurry that was briefly heated to reflux, then was cooled to room temperature and filtered. The air-dried product was dissolved in 700 ml of 0.1N sodium hydroxide, heated to 80° C and filtered (no residue). Sodium chloride (270 gm) was added to salt-out the product. This slurry was heated with stirring at 80° C for 3 hours while ammonia evolved. Upon cooling to room temperature, the product was isolated by filtration. This reprecipitation was repeated twice, and the final precipitate was washed with 1.8 liters of 80 percent aqueous ethanol to remove occluded NaCl. A convenient final purification was achieved by washing the blue powder in the thimble of a Soxhlet apparatus with hot 95 percent ethanol for 18 hours. The product was then dried in vacuo for 2 days to give 22.0 gm (54 percent) of the desired CoTSPC as determined by UV-VIS spectroscopy.

2.2 Methanol-Water Solutions.

Reagent-grade methanol and deionized, distilled water were used to make the methanolic aqueous solutions. The composition of these solutions was determined by measuring the density of 5-ml aliquots of each solution. Calibrated volumetric flasks and pipettes were used in these measurements. Appendix A contains details of these determinations.

2.3 Spectrophotometric Measurements.

All spectrophotometric measurements were made in a Beckman Model 25 UV-VIS spectrophotometer, using a 1-cm cell path length. The CoTSPC solutions were equilibrated for at least 30 minutes in a water bath that was also connected to the cell compartment of the instrument. The solution was transferred to the spectrophotometer cell and allowed another 3 to 5 minutes to equilibrate. The temperature of the solution was recorded with the thermocouple in the cell compartment that is integral to the spectrophotometer. This thermocouple was calibrated against an NBS thermometer. The water bath kept the cell compartment temperature within ±0.1° C.

2.4 Determination of Dimerization Constants.

The absorbance of a solution in a 1-cm cell containing only monomer and dimer is

$$A = \epsilon_M [M] + \epsilon_D [D] \tag{1}$$

where A = absorbance,

ϵ_M = molar absorption coefficient, monomer, $M^{-1} cm^{-1}$,

ϵ_D = molar absorption coefficient, dimer, $M^{-1} cm^{-1}$,

[M] = monomer concentration, M, and

[D] = dimer concentration, M.

The equilibrium between monomer and dimer is

$$K = [D]/[M]^2 \tag{2}$$

where K = dimerization constant, M^{-1}.

The total concentration of CoTSPC, [Co], is

$$[Co] = [M] + 2[D] \tag{3}$$

Equations (2) and (3) can be combined to give the monomer concentration in terms of total CoTSPC as

$$[M] = \frac{-1 + \sqrt{1 + 8 K [Co]}}{4K}. \tag{4}$$

With equations (2) and (4), one can rewrite equation (1) in terms of the experimentally accessible total concentration of CoTSPC as

$$A = \epsilon_M \left(\frac{-1 + \sqrt{1 + 8K [Co]}}{4K} \right) + \frac{\epsilon_D}{2} \left[[Co] - \left(\frac{-1 + \sqrt{1 + 8K [Co]}}{4K} \right) \right] \tag{5}$$

In an earlier report,[59] we described a method based on Monahan's technique[60] by which both the monomer and dimer molar absorption coefficients were determined simultaneously. A series of solutions with different CoTSPC concentrations was made with aliquots from a stock solution of CoTSPC. The absorbances of these solutions were measured at 662 nm, the maximum absorbance of the monomer. A nonlinear, least-squares program[61] based on the Gauss-Newton technique was used to fit the measured absorbances versus CoTSPC concentrations to equation (5). The program found best-fit values of ϵ_M, ϵ_D, and K. Absorbance measurements were repeated at various temperatures and mean values of ϵ_M and ϵ_D were determined.

This experiment was repeated with four stock CoTSPC solutions yielding mean values for ε_M and ε_D of 9.6 ±0.6 x 10^4 M^{-1} cm^{-1} and 7.6 ±0.8 x 10^4 M^{-1} cm^{-1}, respectively, with the error representing the sample standard deviation among the four stock solutions. These values of ε_M and ε_D were used to fit absorbances versus [Co] with equation (5) to obtain K.

These same values of ε_M and ε_D were used to compute the dimerization constant of CoTSPC in methanol-water solutions. Both Abel,[52] and Gruen and Blagrove[5] have shown that the molar absorption coefficient of the monomer is unchanged in water and 20 percent by volume solution of methanol-water or ethanol-water. In our earlier report,[59] we measured the monomer's molar absorption coefficient in 20 percent by volume ethanol-water and obtained a value of 1.0 x 10^5 M^{-1} cm^{-1} at λ = 662 nm in a 10^{-7} M solution of CoTSPC. Other reported values for the monomer's molar absorption coefficient are 1.03 x 10^5 M^{-1} cm^{-1} at λ = 663 nm determined by heating a water solution until the absorbance was unchanged,[40] 1.2 x 10^5 M^{-1} cm^{-1} at λ = 663 nm determined by dilution in an ethanol-water solution,[5] and 1.04 x 10^5 M^{-1} cm^{-1} at λ = 662 nm determined by dilution in methanol-water mixtures.[52]

3. RESULTS AND DISCUSSION

3.1 Dimerization of CoTSPC in Water.

Detailed results on the dimerization of CoTSPC were reported earlier.[59] Since the dimerization constants in water are the starting point for discussing the effect of methanol on the dimerization of CoTSPC, the following paragraphs review our results.

Figure 2 illustrates a spectrum of a 1.17 x 10^{-5} M solution of CoTSPC between 600 and 700 nm that was heated to 70° C and allowed to cool to room temperature. The shoulder near 620 nm grew and the peak near 660 nm decreased as more dimer formed at the lower temperature. The presence of the isosbestic point at 634 nm was taken as evidence that only monomer and dimer existed at this concentration. To avoid interference from higher aggregates, subsequent stock solutions were made no more concentrated than 1.2 x 10^{-5} M.

Table 1 summarizes the dimerization constants measured in pure water, which include dimerization constants measured with fresh stock solutions of CoTSPC in order to check the self-consistency of our method to determine dimerization constants.
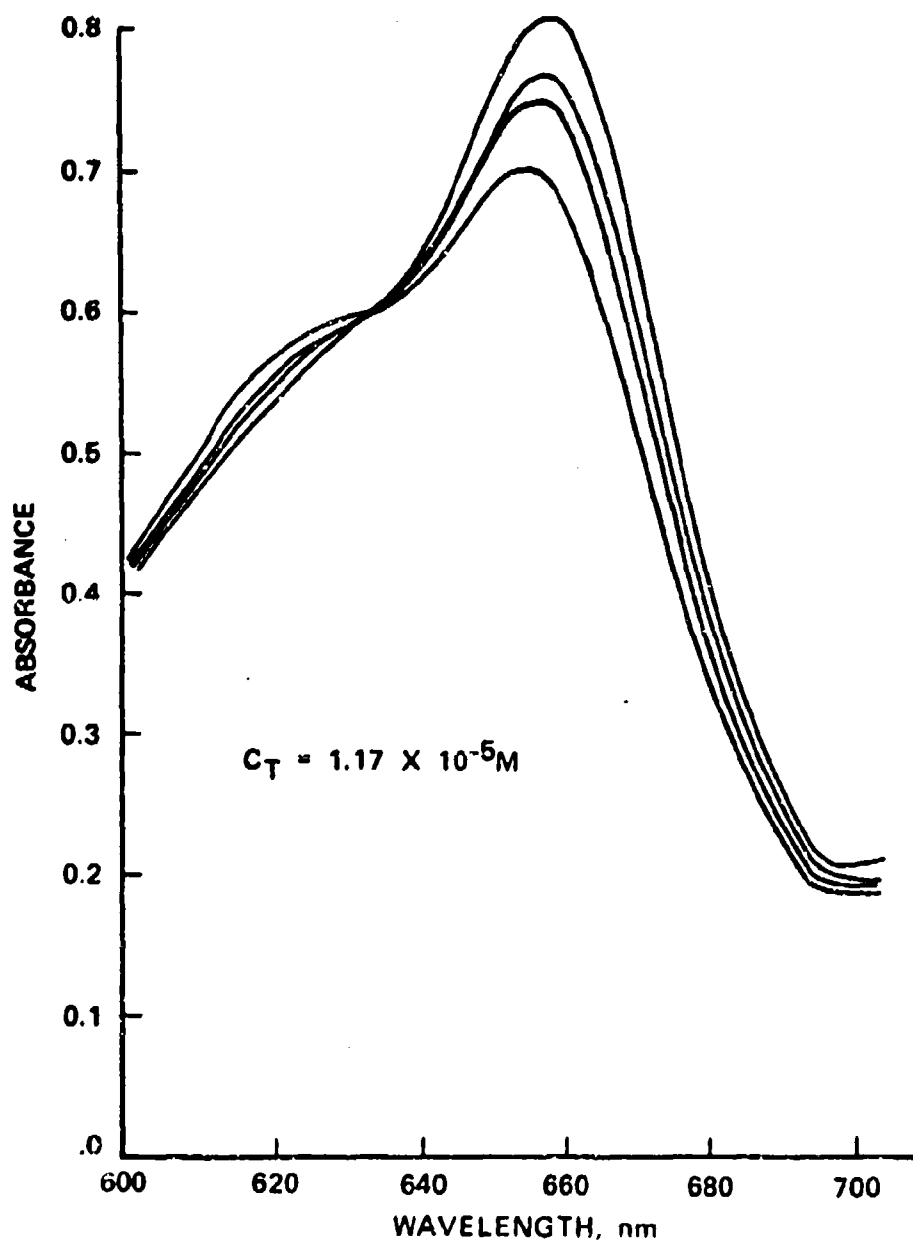
Figure 2.   Absorbance of CoTSPC in Water at Various Temperatures

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Table 1. Dimerization Constants of CoTSPC in Water[a]

T	$K, M^{-1}, X\ 10^{-5}$ [b]	$K, M^{-1}, X\ 10^{-5}$ [c]
°C		
16.1	4.2 ±0.2	---
20.1	2.0 ±0.2	3.1 ±0.1
24.2	2.4 ±0.1	---
24.9	---	2.1 ±0.08
29.6	1.8 ±0.05	1.6 ±0.09
34.2	---	1.2 ±0.07
34.6	1.2 ±0.05	---
41.0	0.81 ±0.04	0.75 ±0.04
45.6	0.60 ±0.03	

[a]Error expressed as sample standard deviation.

[b]Determined with solutions used to establish values for molar absorption coefficients.

[c]Determined with new stock solutions of CoTSPC using $\epsilon_M = 9.6\ x\ 10^4\ M^{-1}\ cm^{-1}$ and $\epsilon_D = 7.6\ x\ 10^4\ M^{-1}\ cm^{-1}$.

Since the dimerization constants were measured in dilute CoTSPC solutions ($10^{-5} - 10^{-6}$ M), one can assume that these dimerization constants represent the thermodynamic equilibrium constants from which the standard free energy, $\Delta F°$, can be determined through the familiar expression

$$\Delta F° = -RT\ \ln(K). \quad (6)$$

The temperature dependence of $\Delta F°$ can then be used to determine the standard-state enthalpy and entropy of dimerization.

Figure 3 illustrates a plot of $\ln(K)$ versus $1/T$ suggesting that the enthalpy is independent of temperature. Values of $\Delta H°$ and $\Delta S°$ were then determined with the nonlinear, least-squares program by fitting the data in table 6 to

$$K = EXP^{(-\frac{\Delta H°}{RT} + \frac{\Delta S°}{R})}. \quad (7)$$

The best-fit values of $\Delta H°$ and $\Delta S°$ are -12.0 ±0.03 kcal/mole and -16 ±1 cal/mole-K, respectively, with the error expressed as the standard deviation of the mean, an output of the program.[61] Table 2 compares dimerization constants calculated with the best-fit values of $\Delta H°$ and $\Delta S°$ with the experimental values. Table 3 lists the results Eyring[41] obtained for the thermodynamics of CoTSPC dimerization from kinetic and spectrophotometric methods at 38, 48, and 58° C.
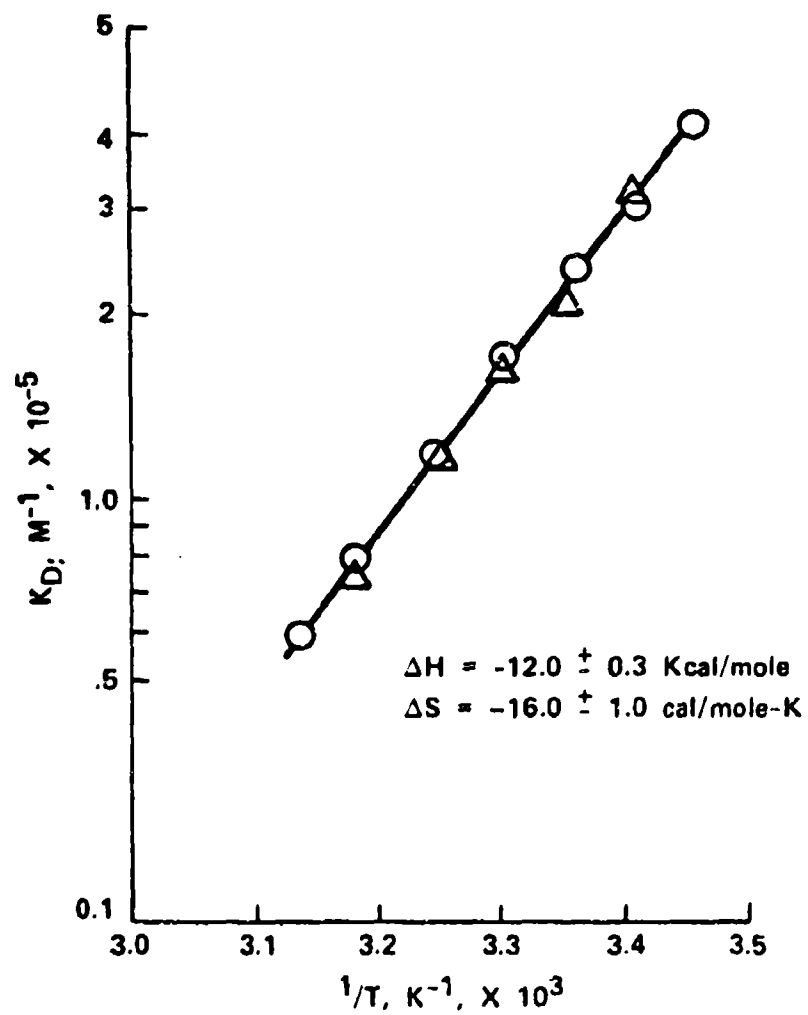
Figure 3. Temperature Dependence of CoTSPC Dimerization Constant in Water

Table 2. Comparison Between Experimental Dimerization Constant With Those Calculated With Best-Fit Activation Parameters[a]

T	K, Exp't	K, Fit
°C	M^{-1}, x 10^{-5}	M^{-1} x 10^{-5}
16.1	4.2	4.1
20.1	3.01; 3.1	3.1
24.2	2.4	2.3
24.9	2.1	2.2
29.6	1.8; 1.6	1.6
34.2	1.2	1.2
34.6	1.2	1.2
41.0	0.81; 0.75	0.78
45.6	0.60	0.59

[a] $\Delta H° = -12.0 \pm 0.3$ kcal/mole; $\Delta S° = -16 \pm 1$ cal/mole - K.

Table 3. Thermodynamic Parameters for CoTSPC Dimerization in Water

$\Delta H°$	$\Delta S°$	Method	Reference
kcal/mole	cal/mole-K		
-12.6 ± 1.3[a]	-14 ± 4[a]	ratio of rate coefficients	41
-14 ± 0.9[a]	-18 ± 3[a]	spectrophotometric	41
-12.3 ± 0.3[a]	-16 ± 1[b]	spectrophotometric	this work

[a] Error estimated by authors.

[b] Standard deviation of the mean.

3.2 Dimerization Constants in Methanol-Water Solutions.

Table 4 lists the composition of the methanol-water solutions as determined by density measurements.

Figure 4 illustrates the spectra of CoTSPC dissolved in these solutions between 600 and 700 nm where the peak near 660 nm grows as methanol concentration increases. The isosbestic point at 634 nm is indicative of a two-state equilibrium as well as the insensitivity of the molar absorption coefficients to methanol.

The experiments were performed in triplicate with three Co stock solutions labelled A, B, and C yielding CoTSPC concentrations of 4.92×10^{-6} M, 5.09×10^{-6} M, and 5.14×10^{-6} M, respectively, after dilution in methanol-water solutions. The remaining results for the other temperatures are listed in Appendix B.

Table 5 lists the absorbances measured for methanol-water solutions at 15.7° C along with the dimerization constants computed from equation (5) with ϵ_M and ϵ_D fixed at 9.6×10^4 M^{-1} cm^{-1} and 7.6×10^4 M^{-1} cm^{-1}, respectively.

Table 6 summarizes the dimerization constants measured in methanol-water. One sees a steady decrease in the dimerization constant with increasing temperature or with increasing methanol content. This trend be made more evident through a plot of $\Delta F°$ versus methanol mole as shown in figure 5. The values in pure water at these temperatures are calculated from the $\Delta H°$ and $\Delta S°$ determined previously[59] (table 7).

Abel and coworkers[52] interpreted the steady decrease in aggregation with increasing methanol as evidence for the specific interaction of water in the CoTSPC dimer as expressed by

$$K = [D]/[M]^2 \cdot [H_2O]^n \qquad (8)$$

where n was found to be 12 for both methanol-water and ethanol-water solutions from plots of $\ln(K)$ versus $\ln(H_2O)$.

The dimerization constants in table 6 were also fit with a linear, least-squares program to

$$\ln(K) = a + b \ln[H_2O] \qquad (9)$$

Table 8 summarizes the slopes determined at the various temperatures. One sees that the slopes are larger than Abel obtained, and the slopes vary with temperature. One might have expected n to be independent of temperature. A further test of Abel's hypothesis will be made through the determination of the enthalpy and entropy of dimerization in the methanol-water solutions. If the role of methanol is simply to dilute the water available to interact with the monomer, the enthalpy of dimerization should not vary as one adds methanol. The next section addresses the temperature dependence of CoTSPC dimerization in methanol-water.

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Table 4. Composition of Methanol-Water Solutions

Nominal Volume of MeOH,ml	Volume of Solution,ml	Density of Solution,g/ml	Mass of MeOH,g	Mass of Water,g	Mole of MeOH	Moles of Water	Mole Fraction of MeOH	Molar Vol. ml/mole	Excess Vol. ml
1	99.99	0.9965	0.787	98.86	0.0245	5.492	0.00444	18.13	0.16
2	99.85	0.9939	1.56	97.68	0.0487	5.427	0.00869	18.24	0.10
4	99.98	0.9913	3.15	95.96	0.0983	5.331	0.0181	19.42	0.27
6	99.97	0.9881	4.72	94.06	0.147	5.226	0.0274	.01	0.36
8	99.98	0.9845	6.29	92.16	0.196	5.119	0.0369	18.81	0.42
9	99.95	0.9820	7.07	91.08	0.221	5.060	0.0418	18.93	0.37
10	99.97	0.9837	7.84	90.50	0.245	5.028	0.0465	18.96	0.75
12	99.81	0.9803	9.40	88.44	0.293	4.913	0.0563	19.17	0.83
15	99.85	0.9751	11.77	85.59	0.367	4.755	0.0717	19.49	0.94
20	99.82	0.9687	15.67	80.89	0.489	4.494	0.0981	20.03	1.20

[a] Computed using density of 0.997 g/ml for water and 0.788 g/ml for methanol.

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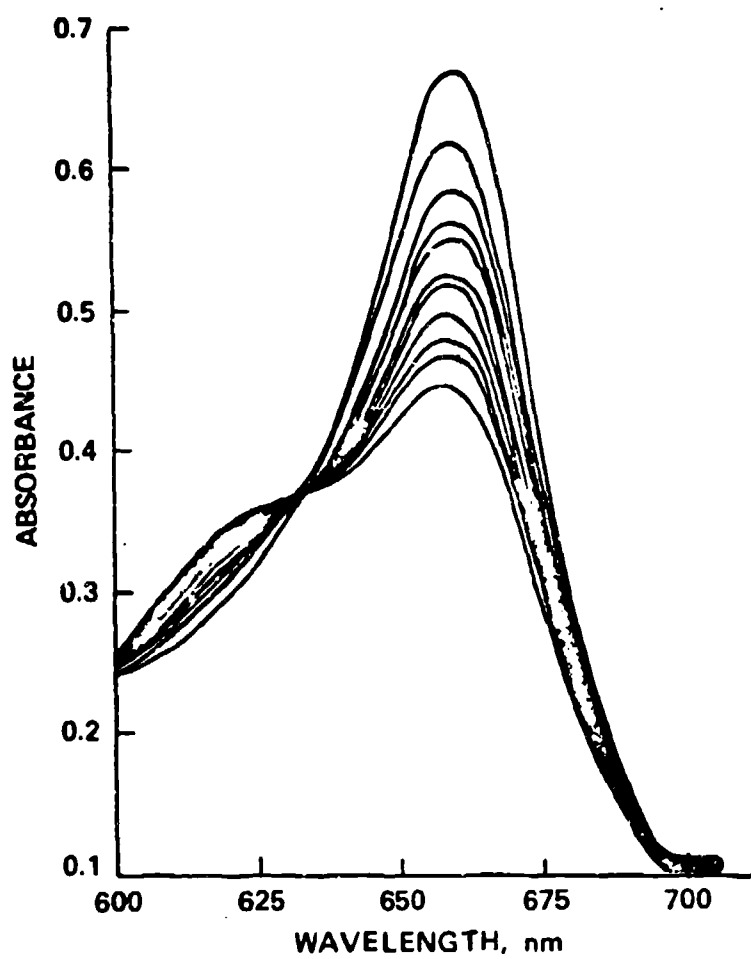
Figure 4. Absorbance of CoTSPC in Various Methanol-Water Solutions

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Table 5. Absorbances and Dimerization Constants Measured at 15.7° C

Solution	Absorbance, λ = 662nm			Dimerization Constant, $M^{-1} \times 10^{-5}$		
	A	B	C	A	B	C
Mole Percent MeOH						
0.444	0.304	0.315	0.319	3.57	3.38	3.58
0.889	0.310	0.317	0.327	3.13	3.24	3.01
1.81	0.310	0.331	0.339	2.26	2.41	2.35
2.74	0.334	0.347	0.355	1.88	1.75	1.71
3.69	0.349	0.358	a	1.39	1.41	a
4.18	0.354	0.367	0.370	1.25	1.18	1.28
4.65	0.362	0.376	0.386	1.07	0.992	0.938
5.63	0.378	0.391	0.398	0.770	0.737	0.742
7.17	0.401	0.411	0.421	0.470	0.487	0.462
9.81	0.437	0.450	0.458	0.178	0.180	0.180

aNot determined.

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Table 6. Dimerization Constants for CoTSPC in Methanol-Water Solutions

	Temperature, °C						
	15.7	20.1	25.0	28.4	34.4	40.5	44.5
Mole Percent MeOH	Dimerization Constants, $M^{-1} \times 10^{-5}$[a]						
0[b]	4.23	3.0	2.21	1.76	1.19	0.816	0.641
0.444	3.51 ±0.1	2.56 ±0.1	1.82 ±0.02	1.40 ±0.02	1.06 ±0.03	0.740 ±0.03	0.612
0.889	3.12 ±0.1	2.33 ±0.1	1.64 ±0.01	1.22 ±0.02	0.927 ±0.03	0.615 ±0.012	0.502
1.81	2.34 ±0.08	1.72 ±0.09	1.20 ±0.01	0.903 ±0.014	0.686 ±0.04	0.480 ±0.008	0.399
2.74	1.78 ±0.09	1.32 ±0.04	0.880 ±0.03	0.656 ±0.06	0.491 ±0.03	0.351 ±0.02	0.295
3.69	1.40 ±0.1	0.933 ±0.04	0.620 ±0.04	0.460 ±0.03	0.332 ±0.03	0.227 ±0.017	0.190
4.18	1.24 ±0.05	0.852 ±0.05	0.554 ±0.01	0.417 ±0.01	0.295 ±0.01	0.206 ±0.004	0.166
4.65	1.00 ±0.08	0.705 ±0.02	0.459 ±0.008	0.354 ±0.001	0.249 ±0.001	0.166 ±0.005	0.137
5.63	0.750 ±0.02	0.474 ±0.05	0.316 ±0.01	0.245 ±0.005	0.178 ±0.008	0.125 ±0.003	0.101
7.17	0.473 ±0.013	0.293 ±0.02	0.195 ±0.098	0.140 ±0.008	0.100 ±0.002	0.0634 ±0.003	0.051
9.81	0.179 ±0.001	0.845 ±0.02	0.049 ±0.004	0.033 ±0.007	0.017 ±0.002	0.003 ±0.003	---

[a]Errors expressed as sample standard derivation.

[b]Computed with $\Delta H° = -11.95$ and $\Delta S° = -15.62$.
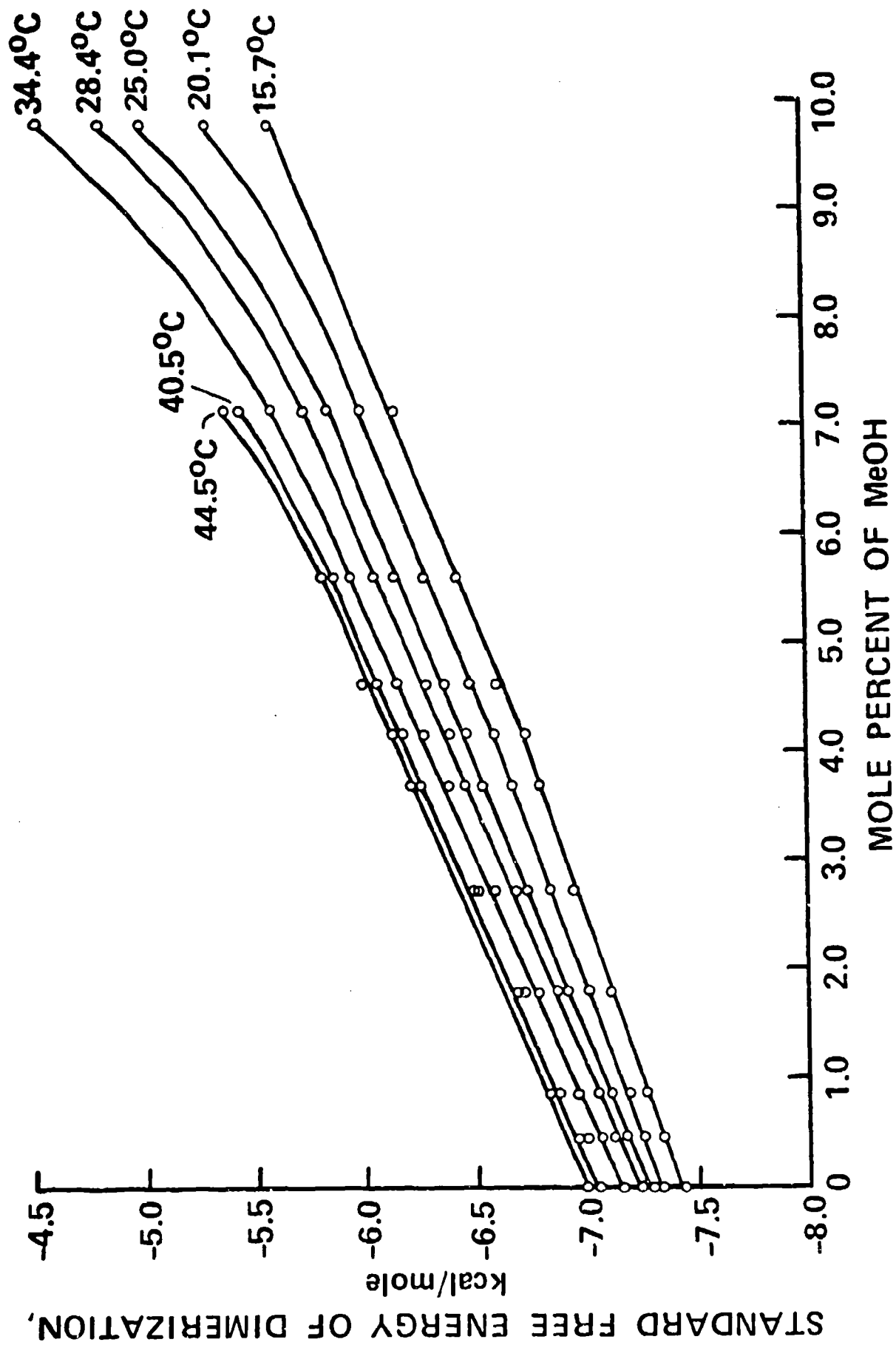
Figure 5. Standard Free Energy of Dimerization of CoTSPC Versus
Mole Percent Methanol

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Table 7. Dimerization Constants of CoTSPC in Water at
Temperatures Used in Methanol-Water Experiments

K, M^{-1}, x 10^{-5} [a]	$-\Delta F^\circ$	$-T\Delta S^\circ$	T
	Kcal/mole	Kcal/mole	°C
4.23	7.44	4.51	15.7
3.10	7.34	4.58	20.1
2.21	7.29	4.66	25.0
1.76	7.24	4.71	28.4
1.19	7.15	4.80	34.4
0.816	7.05	4.90	40.5
0.641	6.99	4.96	44.5

[a]Calculated with ΔH° = -11,947 cal/mole and ΔS° = -15.616 cal/mole-K.

Table 8. Slopes From Plots of ln(K) Versus ln(H$_2$O)
at Various Temperatures[a,b]

T	Slope
°C	
15.7	14.5 ±0.3
20.1	16.4 ±0.6
25.0	17.2 ±0.6
28.4	17.7 ±0.7
34.4	18.9 ±1.1
40.5	23.2 ±3
44.5	16.3 ±0.6

[a]Error is standard deviation of the mean.

[b]Best-fit values of lnK from least-squares fit of lnK versus ln(H$_2$O)
are listed in appendix C.

3.3 Temperature Dependence of Dimerization Constant of CoTSPC in Methanol-Water Solutions

Figure 6 illustrates a plot of ln(K) versus 1/T for the data from
table 6. It is evident from figure 6 that the data for the methanol-water
solutions are curved, which is indicative of a non-zero heat capacity for
the dimerization. To test this trend more quantitatively, we have elected
to treat the dimerization constants with an expression devised by Blandamer,
Robertson and coworkers. Blandamer and coworkers have questioned the
physical significance of values obtained from least-squares treatment of the
temperature being fit have unit correlation coefficients.[62] They propose
the following expression[63] for determining activation parameters as well as
checking the temperature dependence of $\Delta H°$:

$$K = K_o \, EXP \left\{ \frac{\Delta H°}{R} \left(\frac{1}{T_o} - \frac{1}{T} \right) + \frac{\Delta C_p^o}{R} \left[\ln \left(\frac{T}{T_o} \right) + \frac{T_o}{T} + 1 \right] \right\} \qquad (10)$$

where K = equilibrium constant at T,

K_o = equilibrium constant at T_o,

ΔH_o = standard enthalpy at T_o, and

ΔC_p^o = standard heat capacity.

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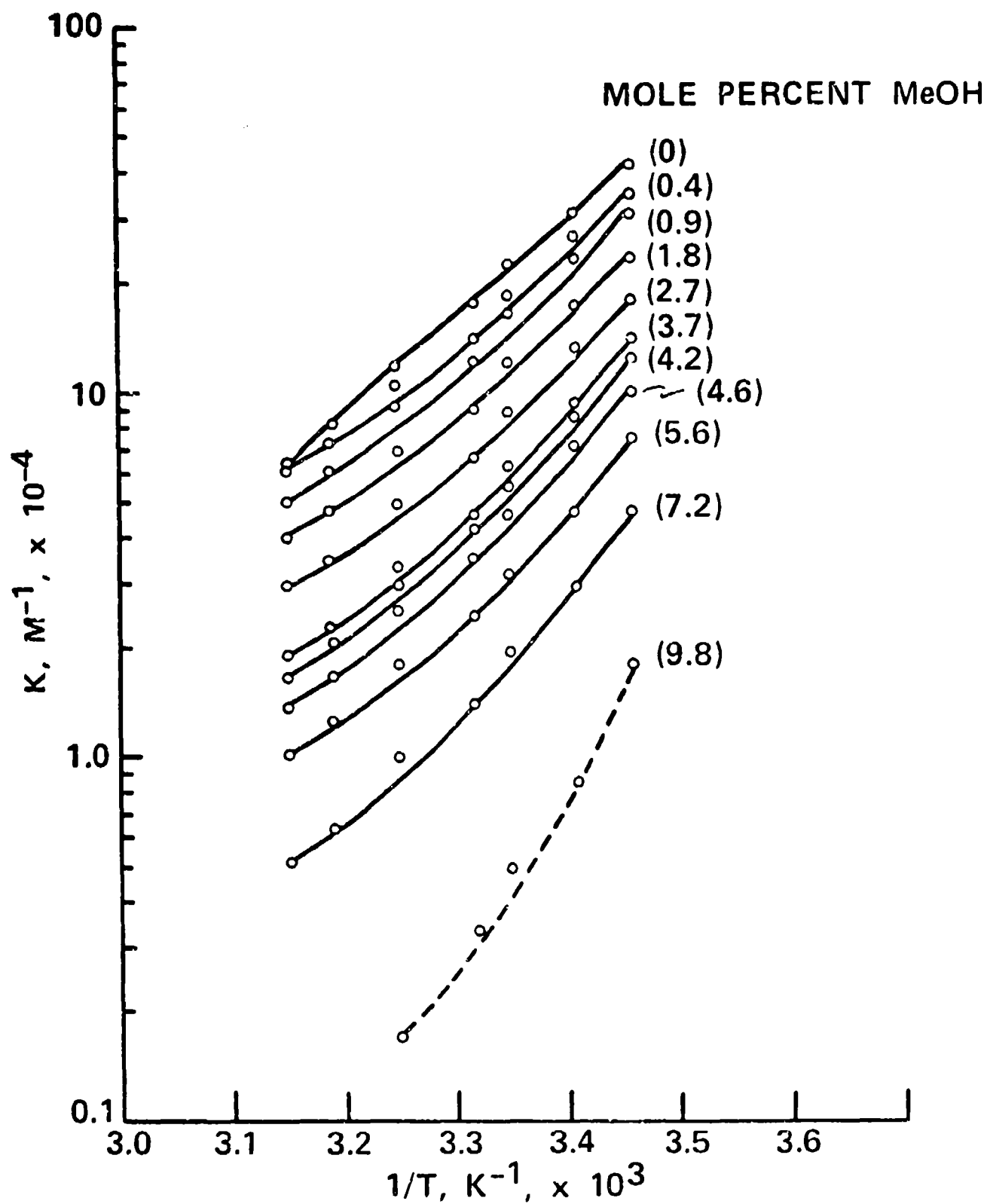
Figure 6. Temperature Dependence of CoTSPC Dimerization Constant in Methanol-Water Solutions

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This equation is obtained from integration of the vant Hoff isochore between T_0 and T, assuming ΔC_p° is independent of temperature. The quantities, K and K_0, are equilibrium constants at T and T_0, respectively; and ΔH° is the enthalpy at T_0. For a set of K and T data, any pair are selected as K_0 and T_0, and the remaining values fit to equation (10) to find best-fit values of ΔH° and T_0 and ΔC_p°. The calculation is repeated with new values of K_0 and T_0 until values of ΔH° and ΔC_p° have been obtained for each value of T in the data set.

The nonlinear, least-squares program was modified for fitting the K and T data in tables 1 and 6 to equation (10) in which ΔH° and ΔC_p° were parameters to be fit while K_0 and T_0 were inserted as fixed parameters. Table 9 summarizes the results of determination of ΔH° and ΔC_p° for the dimerization of CoTSPC in water. One sees that the enthalpy is independent of temperature, and the mean value of ΔH°, -12.0 ± 0.6 kcal/mole (error representing sample standard deviation), is identical to the value of -12.0 ± 0.3 kcal/mole obtained from the fitting the K and T data to equation (7).

Table 9. Results of Calculations to Determine ΔH° for
CoTSPC Dimerization in Water With Equation (10)

T °C	ΔH° kcal/mole	ΔCp° cal/mole-K
16.1	-12.4 ±0.6*	28 ±68*
20.1	-11.2 ±0.8	54 ±95
24.2	-11.1 ±0.7	-156 ±117
24.9	-12.3 ±1.0	154 ±151
29.6	-11.4 ±0.5	-230 ±118
34.2	-12.2 ±0.7	- 39 ±117
34.6	-12.0 ±0.7	- 63 ±108
40.1	-12.7 ±0.8	- 80 ±87
45.6	-12.6 ±0.7	- 53 ±62

*Error represents standard deviation of the mean.

Table 10 lists the results for the 0.44 mole percent methanol solution. The heat capacity is clearly non-zero and not constant over the temperature range as shown in figure 7. Similiar results were obtained at each of the other temperatures, the results of which are collected in Appendix D.

Table 10. Temperature Dependence of ΔC_p^o by Blandamer's Method for 0.44 Mole Percent Methanol

T °C	K, exp't, x 10^{-5}	K fit, x 10^{-5}	ΔH^o/cal/mole	ΔC_p^o, cal/mole-K
15.7	3.51	3.48	-13.0 ±0.4[a]	142 ±43[a]
20.1	2.56	2.57	-12.8 ±0.5	178 ±62
25.0	1.82	1.85	-11.8 ±0.4	144 ±56
28.4	1.40	1.48	-11.6 ±0.6	282 ±68
34.4	1.06	1.02	-10.1 ±0.7	111 ±100
40.5	0.740	0.703	-9.4 ±0.6	167 ±61
44.5	0.612	0.556	-8.9 ±0.5	154 ±47

[a]Standard deviation of the mean computed by nonlinear least-squares program.

Since ΔC_p^o appears to be temperature dependent, the next step was to fit the free energy to an expression in which ΔC_p^o is linearly dependent on temperature; such an expression for free energy takes the form of a power series shown below.[64]

$$\Delta F^o = A + BT + CT^2 \tag{11}$$

One computes ΔH^o, ΔS^o, and ΔC_p^o in terms of A, B, and C, in the following manner:

$$\text{Since} \left(\frac{\partial \Delta F^o}{\partial T} \right)_p = \Delta S^o, \text{ and } T \left(\frac{\partial \Delta S^o}{\partial T} \right)_p = \Delta C_p^o, \text{ then} \tag{12}$$

$$\Delta S^o = -B - 2CT, \text{ and} \tag{13}$$

$$\Delta C_p^o = -2CT. \tag{14}$$

The enthalpy is computed from

$$\Delta H^o = \Delta F^o + T\Delta S^o \tag{15}$$
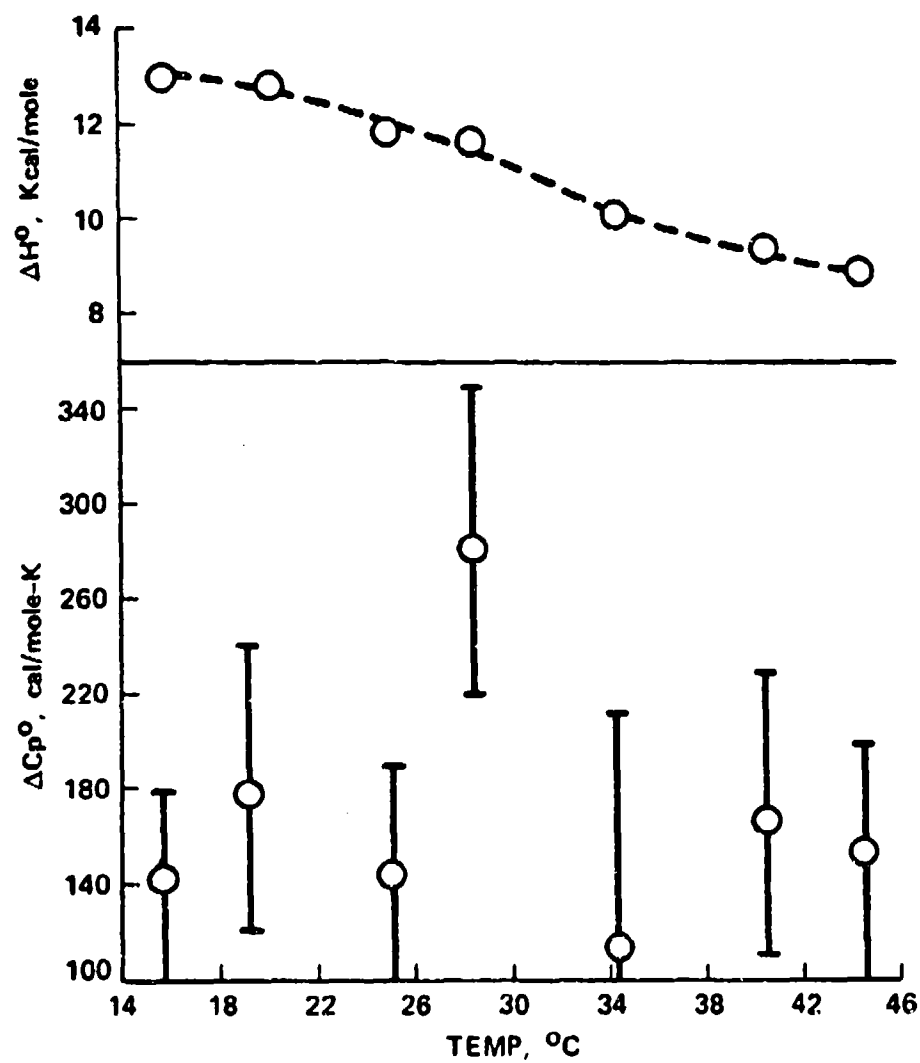
Figure 7. ΔH° and ΔC_p° in 0.44 Mole Percent Methanol-Water by Blandamer's Method

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which becomes

$$\Delta H^\circ = A - CT^2 \qquad (16)$$

The standard free energies of the dimerization constants were fit to equation (11) using the nonlinear, least-squares program. Table 11 summarizes the results of this calculation with the dimerization constants in 0.44 mole percent methanol, where one sees that the values of the dimerization constants from the best fit ΔF° agree well with the experimental values of K. Table 11 also lists the values of ΔH°, ΔS°, ΔC_p°, and $T\Delta S^\circ$ at each temperature. Table 12 summarizes the values of A, B, and C for each methanol-water solution, while Appendix E contains tables equivalent to table 11 for the other methanol-water solutions. It is of interest that Brandts observed a similar temperature dependence for the free energy of denaturation of proteins in ethanol-water solution.[65,66]

Since $-C$ is proportional to ΔC_p°, a plot of $-C$ versus methanol content can be used to see how ΔC_p° varies with methanol. One sees in figure 8 that the heat capacity of dimerization is positive, but irregular. The corresponding enthalpy of dimerization is plotted in figure 9. Such patterns also appear in the excess mixing properties in the "infinitely dilute" solutions of alcohols and water.[67-69] One such property, the excess volume of mixing, can be calculated for the methanol-water solutions in our experiments from the density measurements made to determine the mole fraction of methanol (table 4). Figure 10 is a plot of the excess volume of mixing at 26° C versus methanol. The extrema in figure 10 correspond to maxima and minima in figure 9 for the enthalpy of dimerization at either 25° or 28° C. Helper observed the same irregular features in the thermodynamics of the ionization of acetic and chloroacetic acids in methanol-water mixtures in which extrema in the enthalpy corresponded to extrema in the excess enthalpy of mixing.[70]

Another feature of the thermodynamics of CoTSPC dimerization in methanol, also evident in Helper's experiments, is the compensation between the enthalpy and entropy which leads to small and regular changes in free energy. Compare figure 5, the change in free energy with methanol, with figure 9, the enthalpy versus methanol. Such compensation between ΔH° and ΔS° is also found in mixing alcohol and water,[68,69] as well as in a number of biochemical systems[71] and in micelles.[72] Exner[73,74] has criticized on statistical grounds the validity of assuming compensation exists if a plot of ΔH° versus ΔS° is linear. Instead, Exner contends that compensation is better illustrated by a plot of ln(K) at two seperate temperatures. Figure 11 shows that a plot of ln(K) at 15.7° C versus ln(K) at 40.5° C forms a straight line.

Another view of the effect of methanol on CoTSPC dimerization is to examine the thermodynamic transfer function, ΔX_t°, defined as the difference in a thermodynamic quantity in a mixed solvent minus that in water. Figures 12 through 18 illustrate ΔF_t°, ΔH_t°, and $T\Delta S_t^\circ$ at each temperature studied.

Table 11. Temperature Fit of 0.44 Mole Percent Methanol

T °C	K M⁻¹, x 10⁻⁵	-ΔF kcal/mole	-ΔF Fit kcal/mole	K Fit M⁻¹, x 10⁻⁵	-ΔH° kcal/mole	-ΔS° cal/mole-K	ΔC°p cal/mole-K	-TΔS Kcal/mole
15.7	3.51	7.33	7.33	3.51	12.8	18.8	119	5.4
20.1	2.56	7.26	7.25	2.53	12.2	17.0	121	5.0
25.0	1.82	7.18	7.17	1.81	11.6	14.9	123	4.5
28.4	1.40	7.10	7.12	1.46	11.2	13.5	124	4.1
34.4	1.06	7.07	7.05	1.02	10.5	11.1	127	3.4
40.5	0.740	6.99	6.99	0.743	9.7	8.5	129	2.7
44.5	0.612	6.96	6.96	0.615	9.2	6.9	131	2.2

$A = -29,972 \pm 7040$

$B = 138.0 \pm 46$

$C = -0.2664 \pm 0.076$

Table 12. Parameters for Computing Thermodynamics of CoTSPC
Dimerization in Methanol-Water[a]

Mole Percent MeOH	-A, kcal/mole	B, cal/mole-K	-C, cal/mole-K^2
0.44	29.972[b] ±7.0	138.0[b] ±45	0.2064[b] ±0.076
0.89	21.783 ±1.0	82.2 ±67	0.1106 ±0.11
1.81	34.550 ±8.5	168.4 ±56	0.2540 ±0.09
2.74	44.959 ±9.8	236.8 ±64	0.3644 ±0.11
3.69	52.769 ±6.7	285.5 ±44	0.4375 ±0.07
4.18	47.807 ±6.2	252.7 ±41	0.3826 ±0.07
4.65	38.541 ±6.4	192.0 ±42	0.2820 ±0.07
5.63	55.936 ±9.1	308.5 ±60	0.4747 ±0.1
7.17	48.977 ±1.1	258.6 ±70	0.3821 ±0.1
9.81	86.125 ±4.0	487.8 ±271	0.7237 ±0.4

[a]Errors represent standard deviation of the mean as computed by nonlinear least-squares fit of $\Delta F = A + BT + CT^2$.

[b]Significant figures listed to compute the dimerization constant.
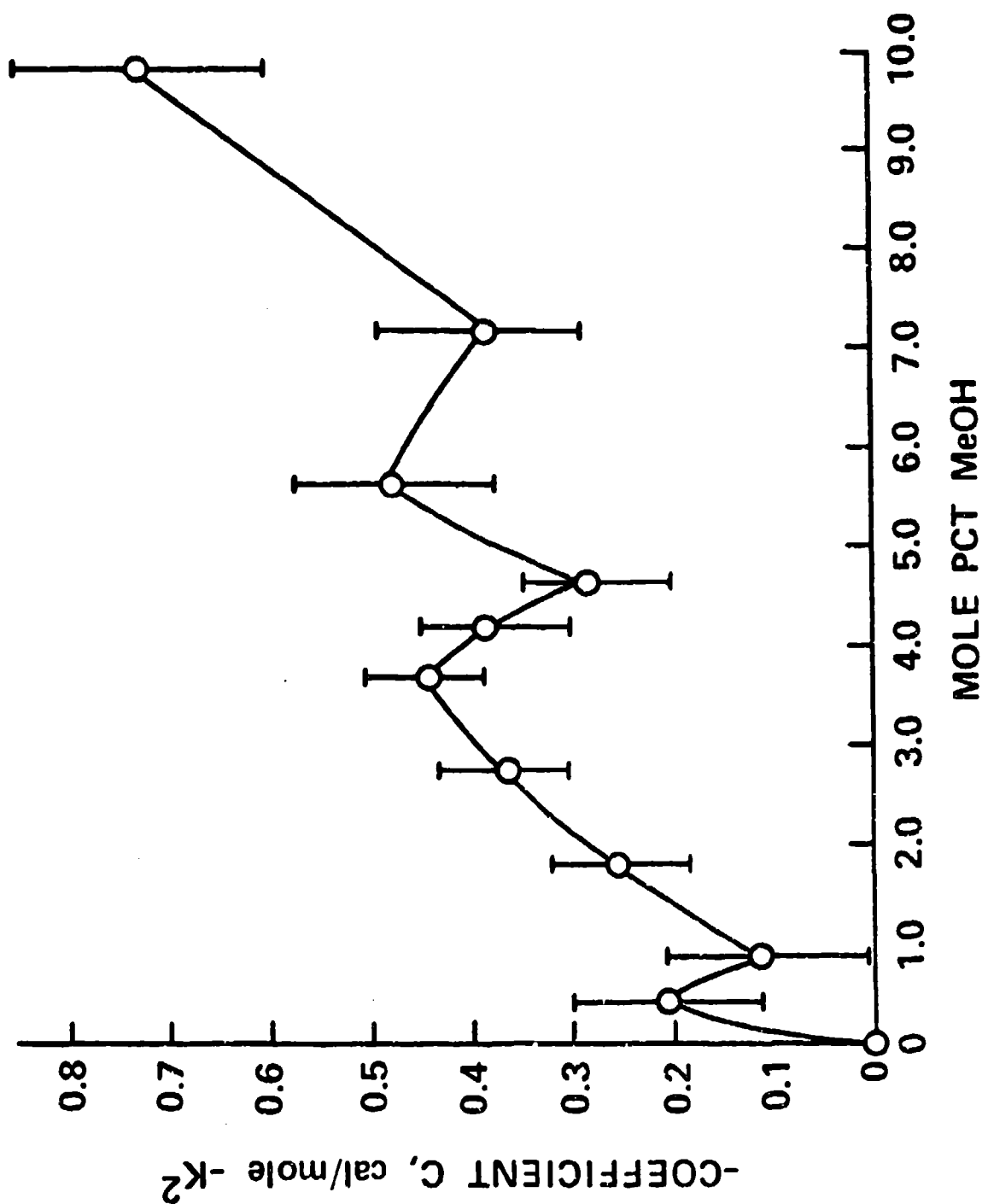
Figure 8.   Variation of C With Mole Percent Methanol
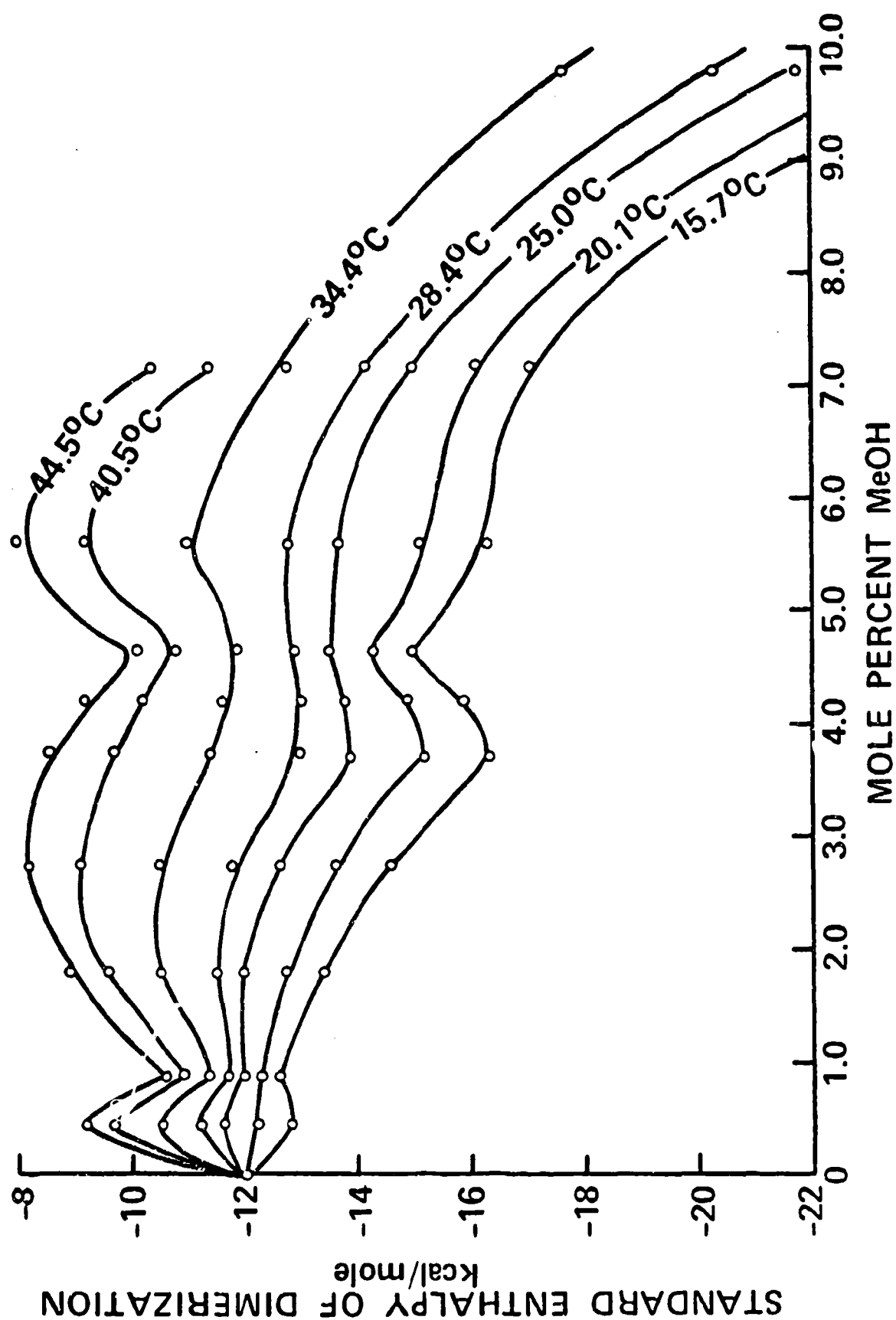
Figure 9. Enthalpy of Dimerization Versus Mole Percent Methanol
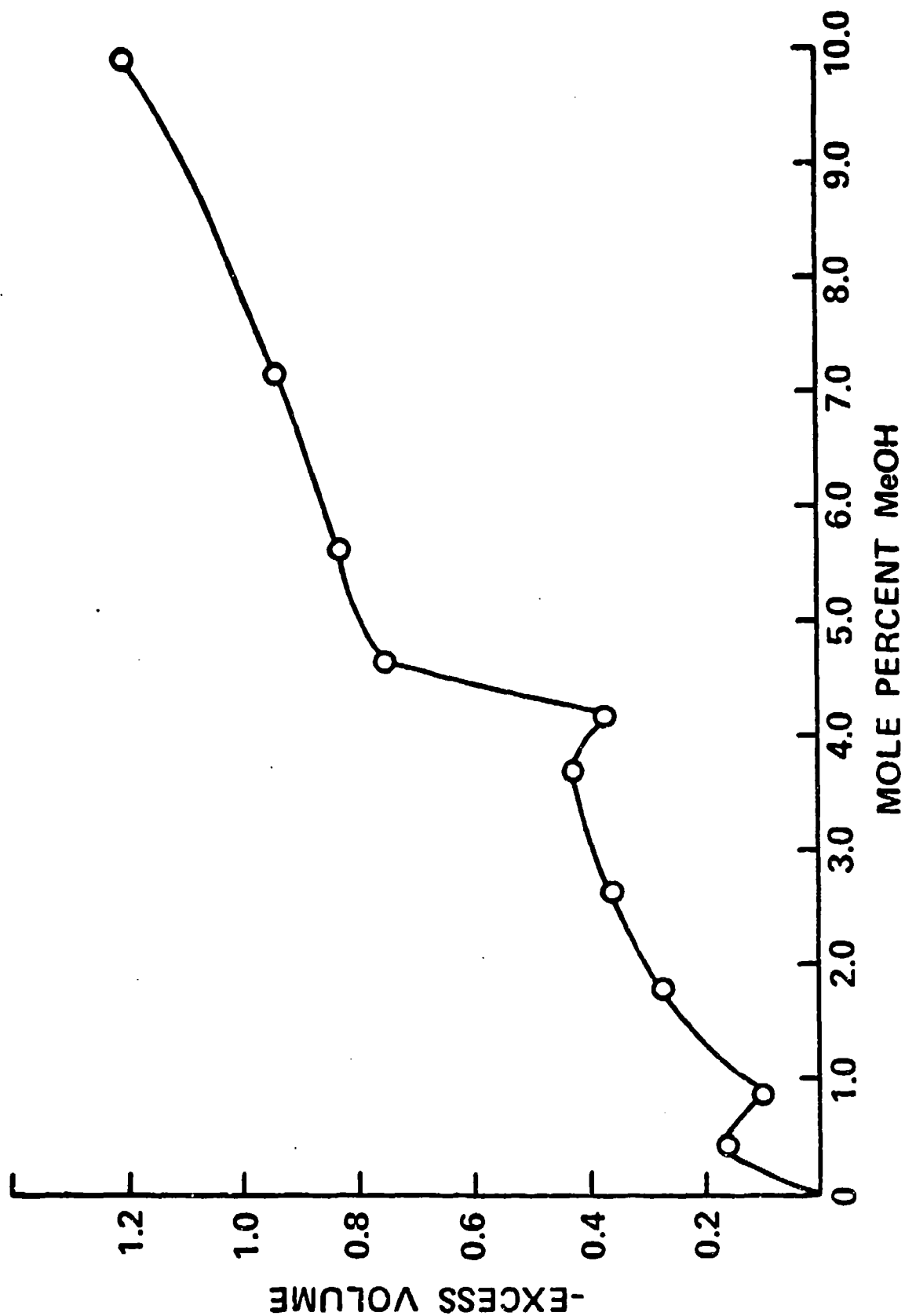
Figure 10.   Excess Volume of Mixing of Methanol-Water Solutions
Versus Mole Percent Methanol

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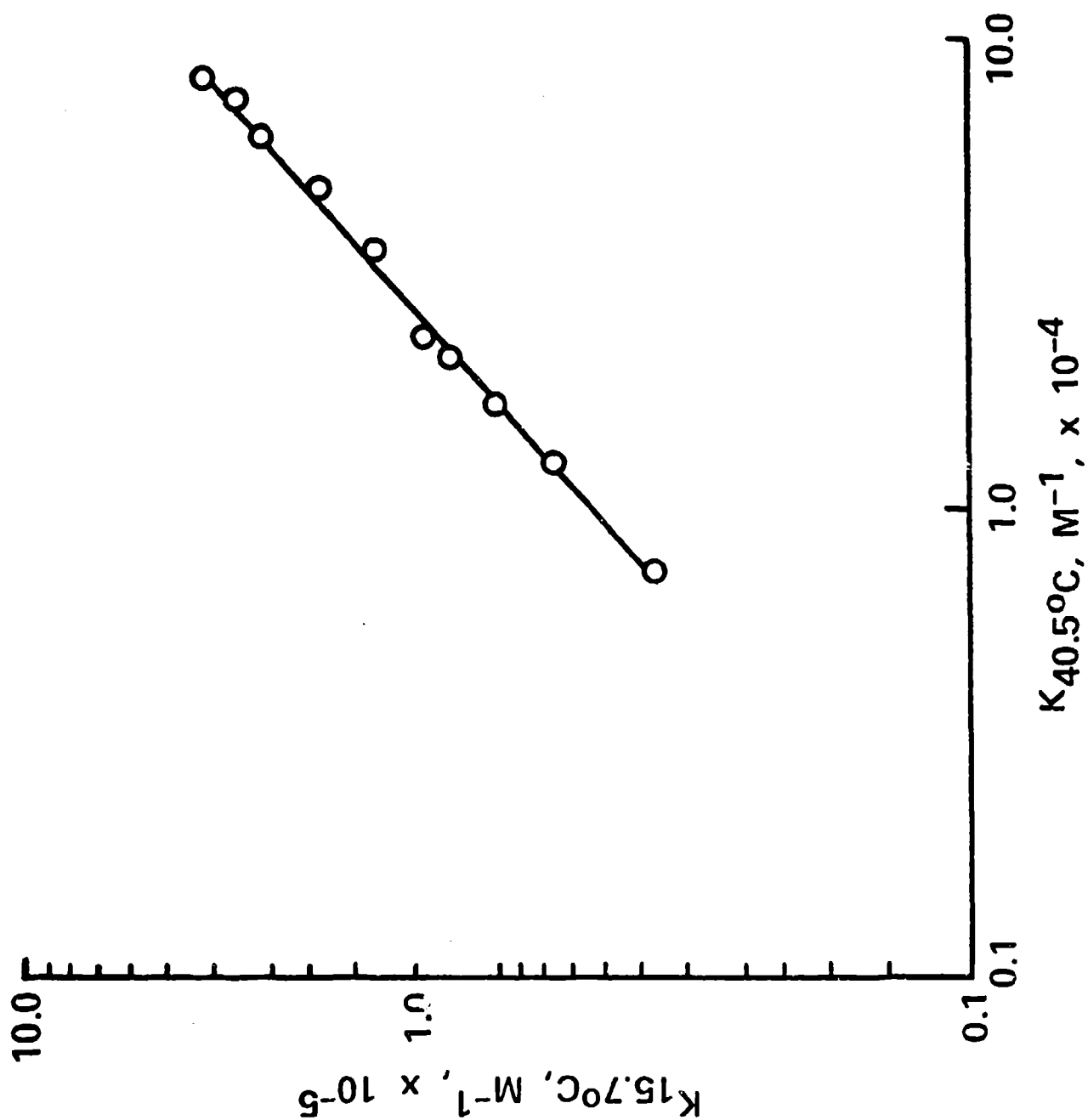
Figure 11. Correlation Between Dimerization Constants in
Methanol-Water Solutions at 15.7° C and 40.5° C
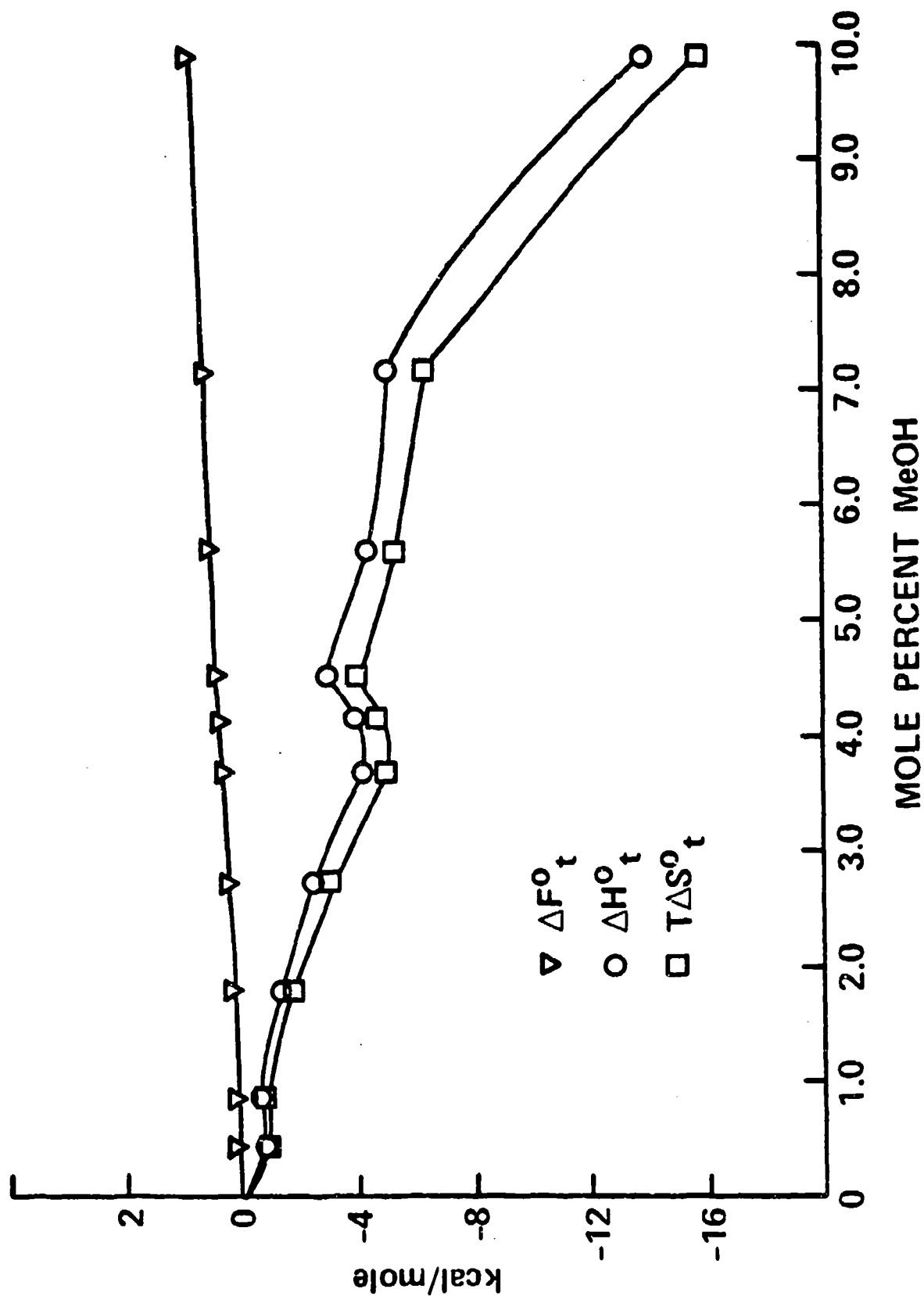
Figure 12.   Thermodynamic Transfer Functions at 15.7° C

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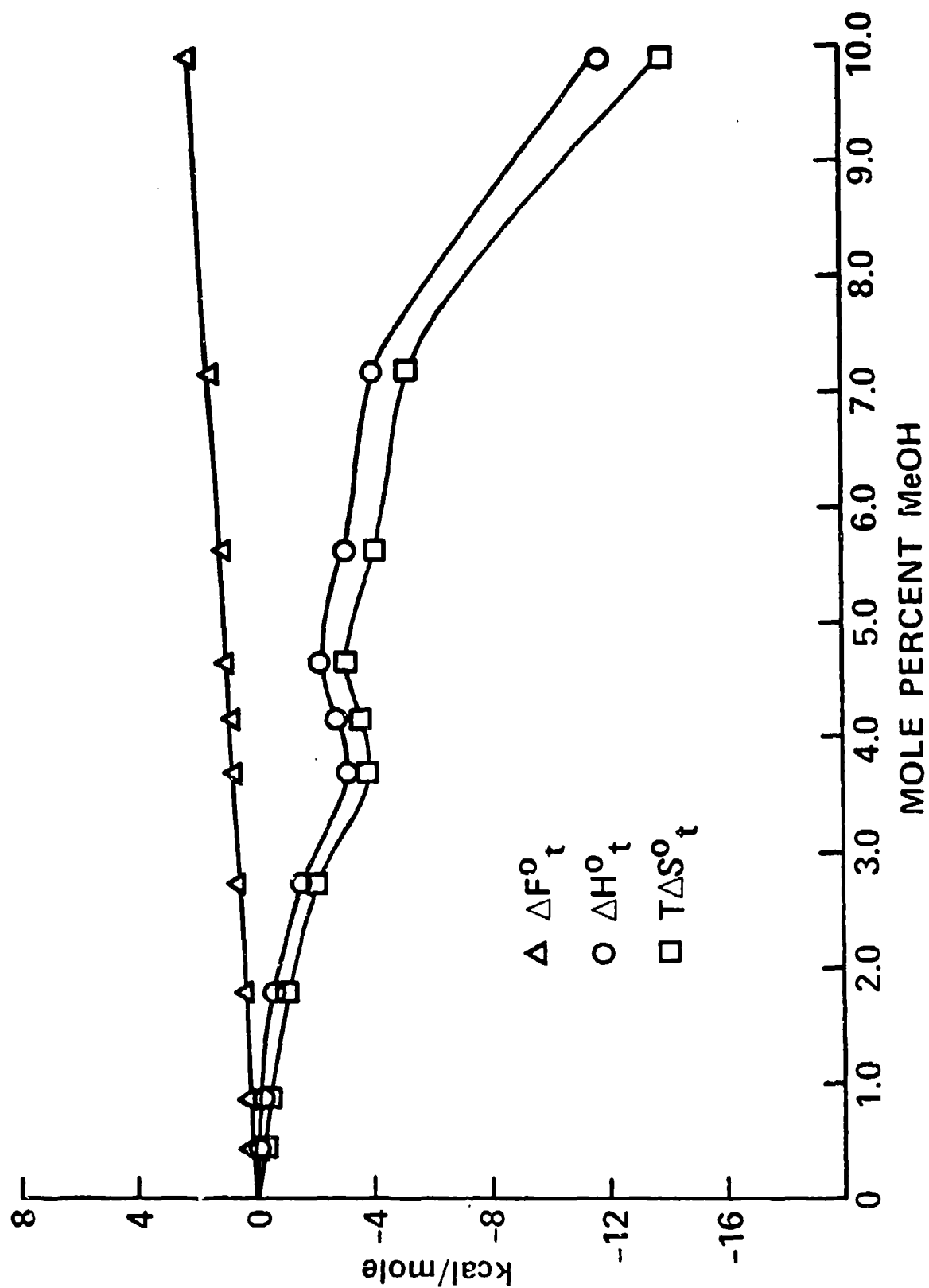
Figure 13. Thermodynamic Transfer Functions at 20.1° C
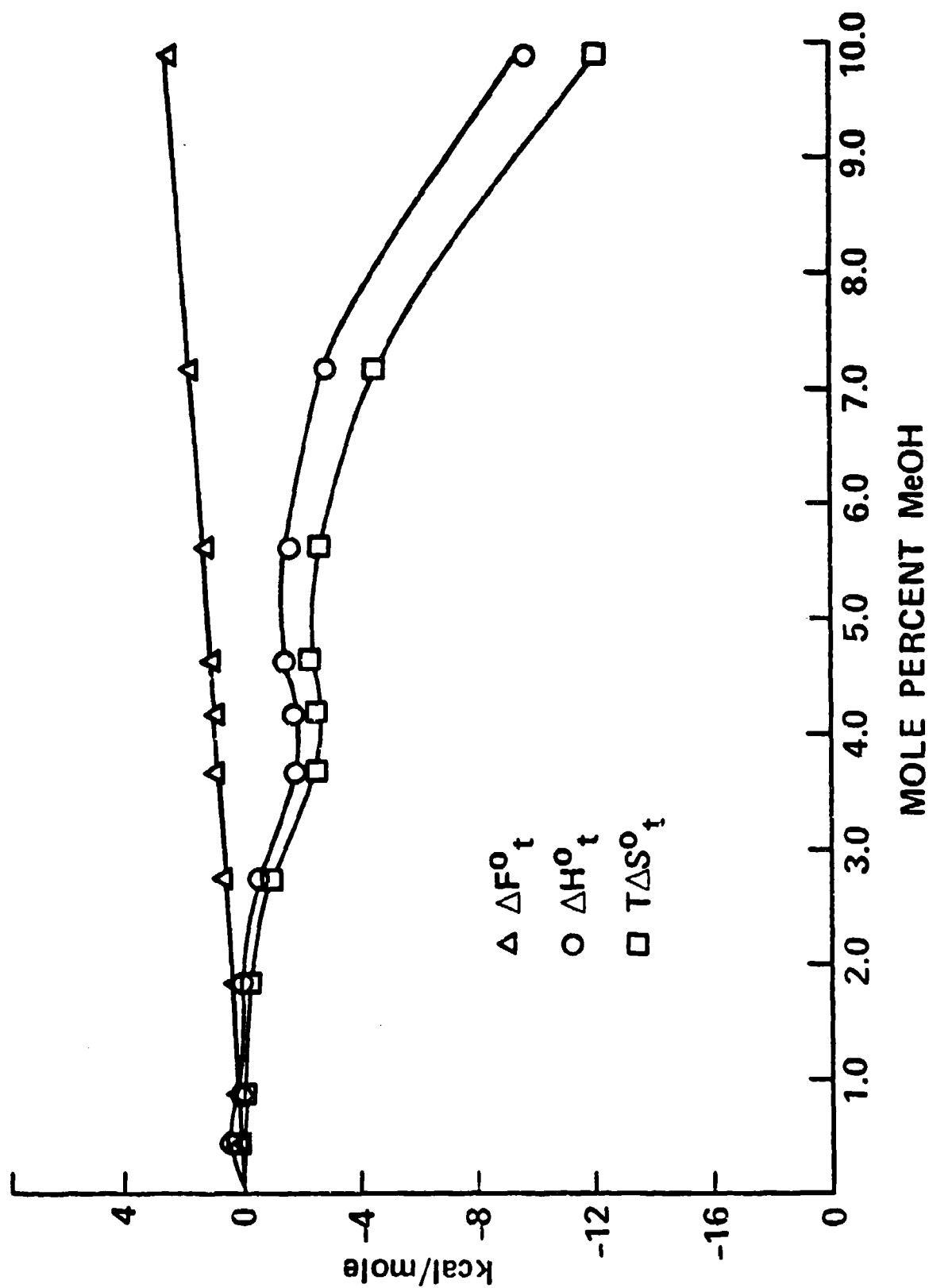
Figure 14. Thermodynamic Transfer Functions at 25.0° C
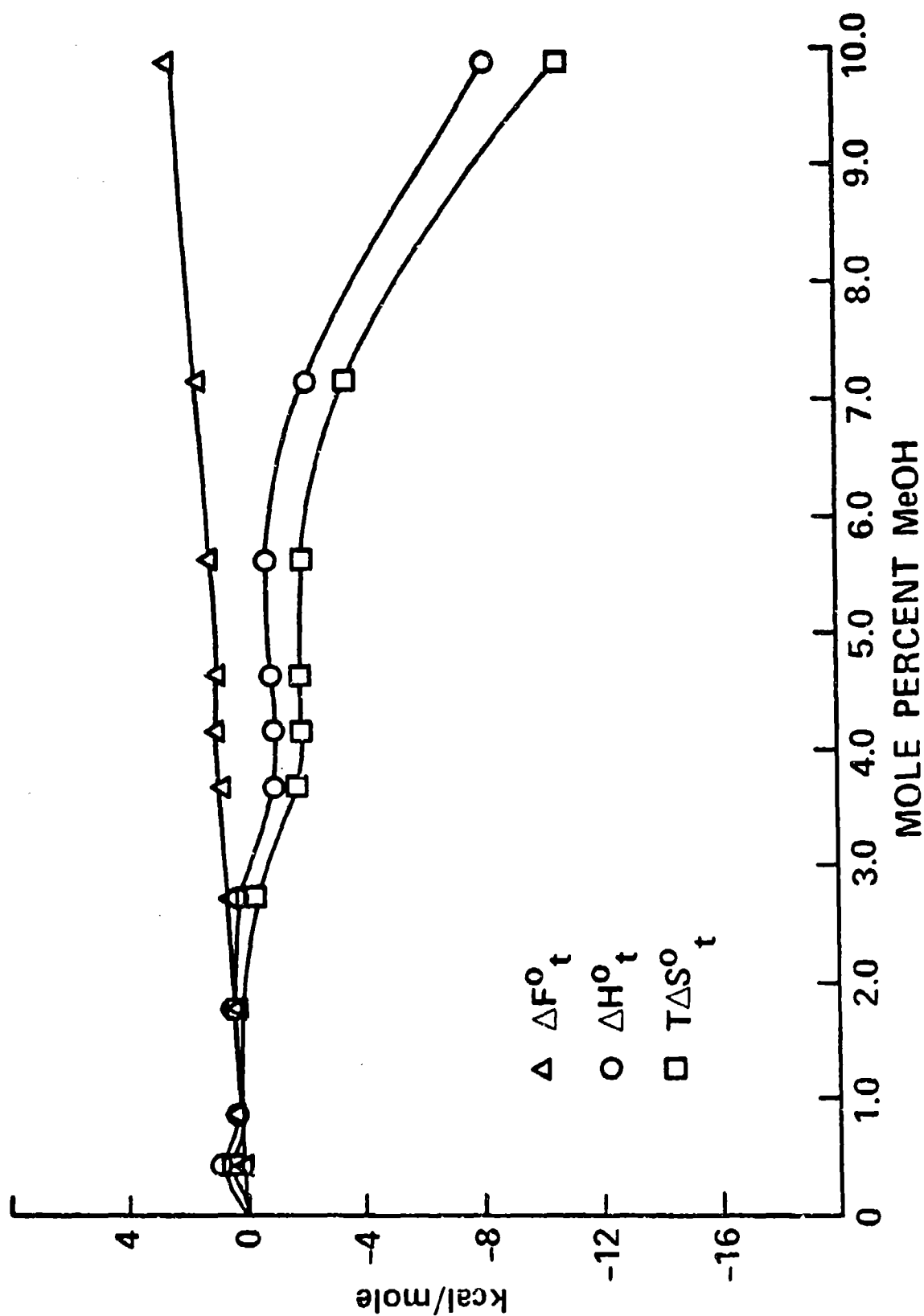
Figure 15. Thermodynamic Transfer Functions at 28.4° C
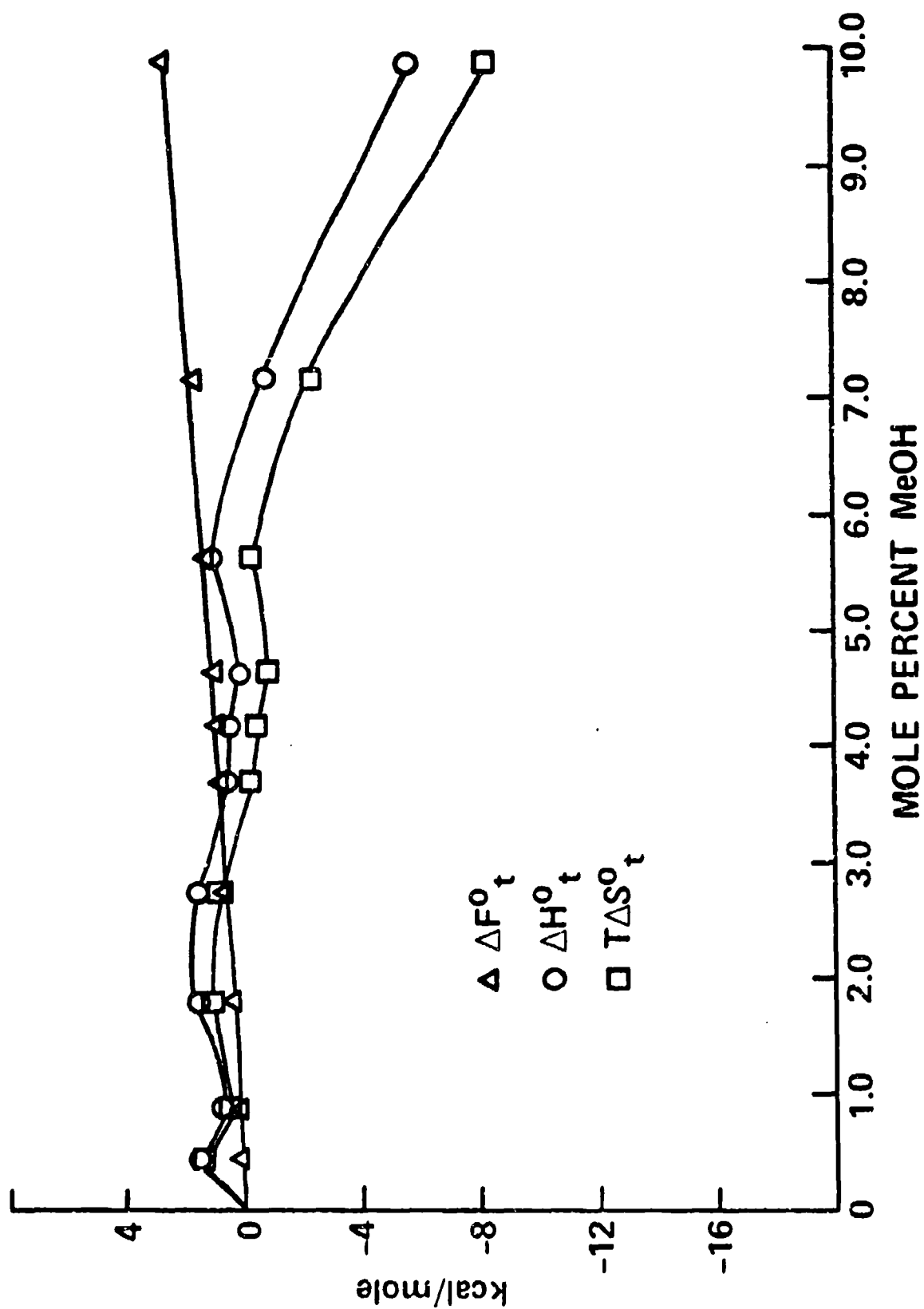
Figure 16. Thermodynamic Transfer Functions at 34.4° C

40
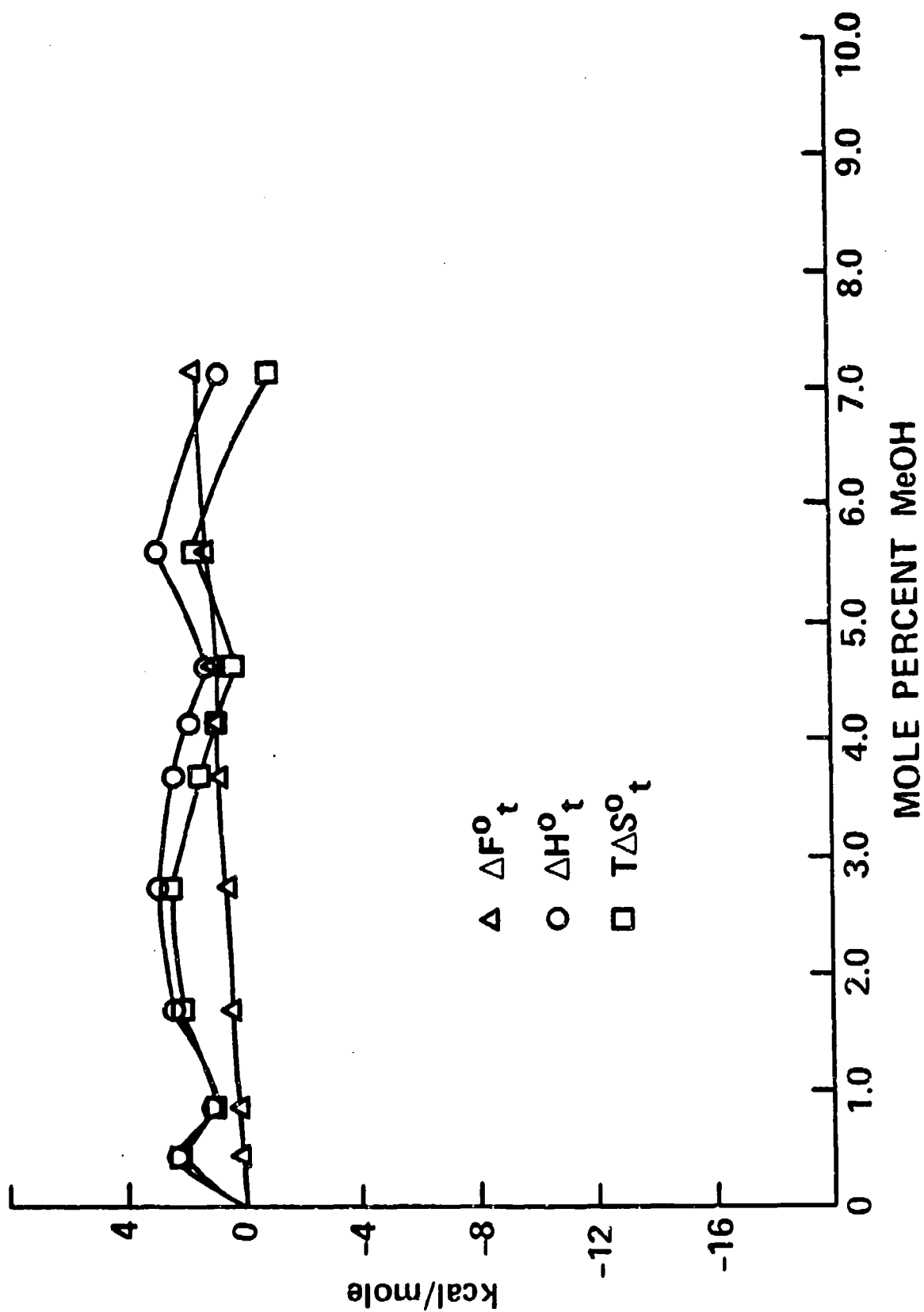
Figure 17. Thermodynamic Transfer Functions at 40.5° C

41
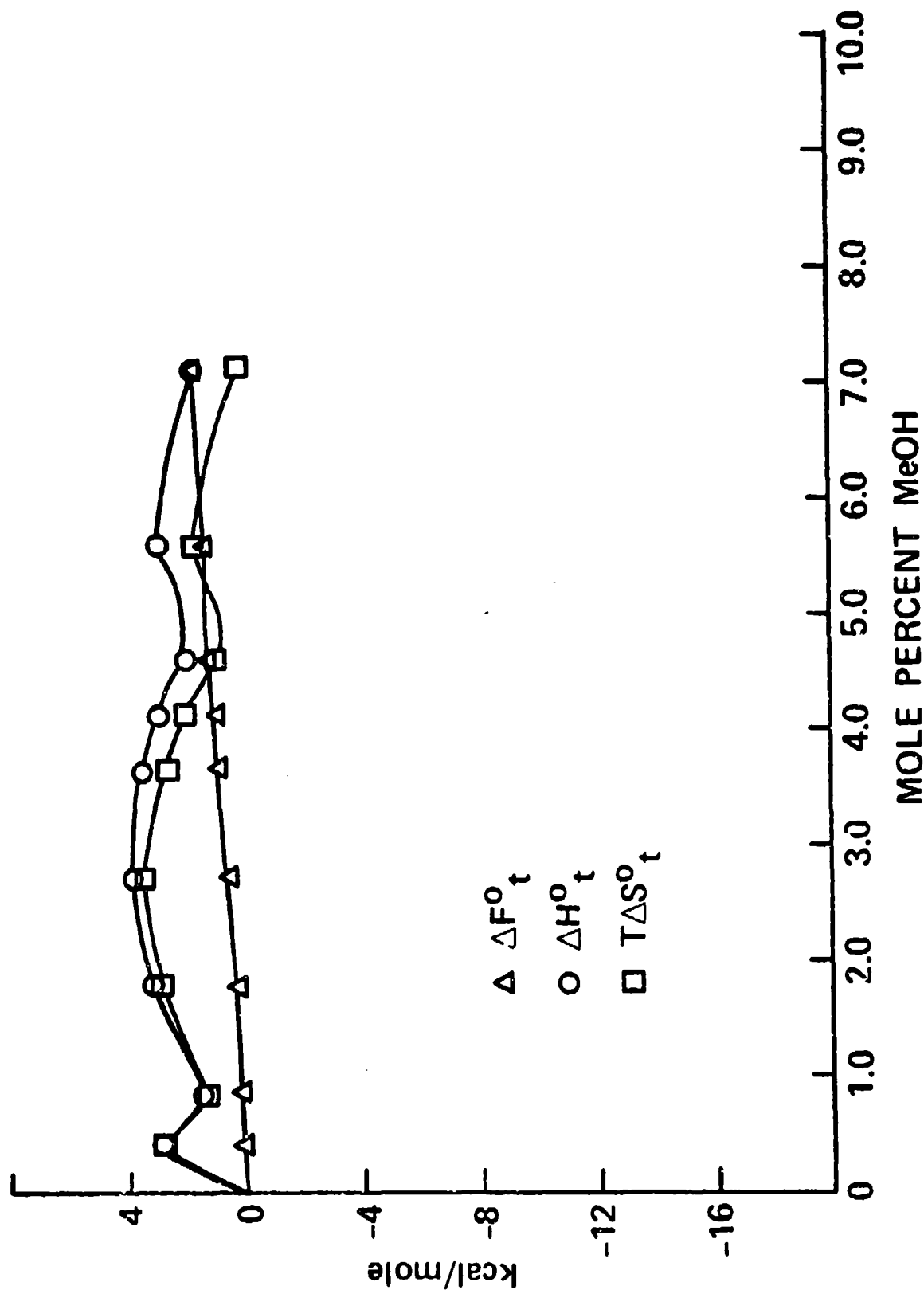
Figure 18.   Thermodynamic Transfer Functions at 44.5° C

One sees that at low temperatures the addition of methanol causes a decrease in both $\Delta H°$ and $T \Delta S°$, but the entropy change slightly dominates leading to a more positive $\Delta F°$ and a smaller value of K. As the temperature is raised, small additions of methanol (<7 mole percent) cause $\Delta H_t°$ and $T \Delta S_t°$ to increase, but with the enthalpy dominant, which still leads to an increase in $\Delta F_t°$ and a corresponding decrease in K relative to that in water.

These trends in ΔH and ΔS can be rationalized in terms of hydrophobic bonding. Formation of a dimer from two monomers is enthalpically favored $(-\Delta H)$, since a bond is formed, but enthropically unfavored $(-\Delta S)$. Since the monomer and dimer are hydrophobic molecules, one must also consider structure-making in the hydration sphere. Since the dimer has less surface exposed to water than the two dimer molecules, the net effect of dimerization is to order less water in the hydration spheres, leading to a $+\Delta S$ and $+\Delta H$ contribution to the overall dimerization process. Methanol is a structure-maker in water, so when the hydrophobic monomer and dimer molecules are placed in methanol-water solution, the monomer does not order as much water in the hydration sphere, and consequently there is less "free" water produced on dimerization. Thus, ΔS_t should be negative; i.e., one is not getting all the positive ΔS contribution from the changes in the hydration sphere as occurred in the absence of methanol. As the temperature increases, the ordered water in the methanol-water solutions "melt." So at higher temperatures, the methanol has less influence on the hydration sphere, and the ΔS in methanol-water is closer to the ΔS in pure water. This is reflected in a positive ΔC_p and in ΔS_t tending toward zero.

Abel's hypothesis would predict that any alcohol will be equally effective in disaggregating the CoTSPC while our own view would suggest that the disaggregation is proportional to the structure-making ability of the alcohol. For a given mole fraction of alcohol, we would predict that longer-chain alcohols will be more effective than methanol, based on the effect of alcohol on the excess volumes of mixing.[69]

Another test of Abel's hypothesis is suggested from figure 19, a plot of free energy versus temperature for different amounts of methanol. The curves for 0.44 mole percent methanol and water appear as if they will cross at a higher temperature, suggesting that small amounts of methanol will stabilize the dimer at such a temperature. Similar behavior has been reported for micelles;[72] alcohol normally raises the critical micelle concentration (CMC), but it has been shown that small amounts of alcohol can lower the CMC at certain temperatures. Under Abel's hypothesis, it would be impossible for alcohol to give a larger value of K than that in pure water.

4. CONCLUSION

Aggregation of CoTSPC in methanol-water solutions has a positive heat capacity of dimerization that is linearly dependent on temperature. Similiar behavior was observed in the denaturation of proteins in alcohol-water mixtures, which was ascribed to the effect of alcohol on hydrophobic bonding.
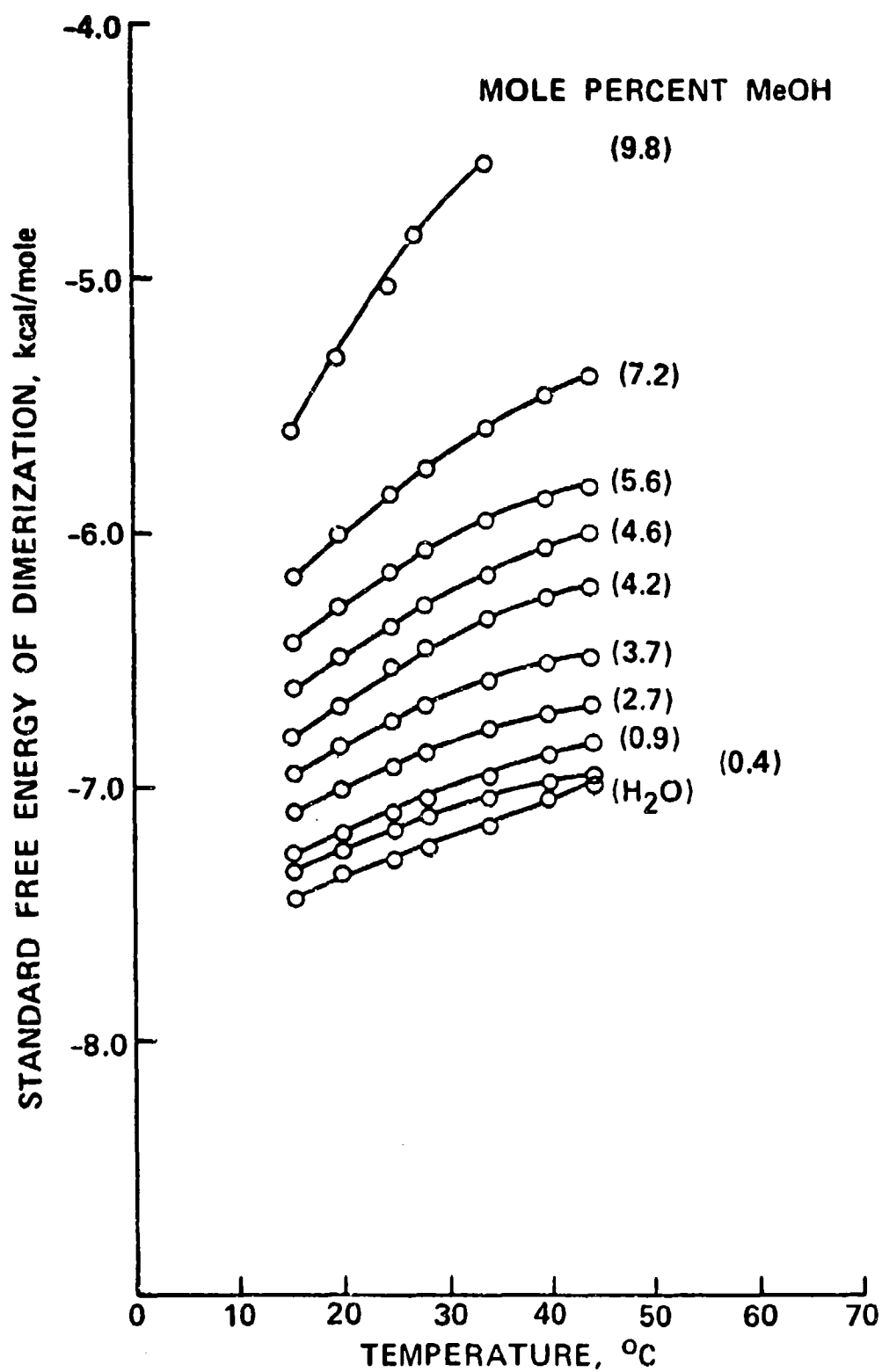
Figure 19. Free Energy of Dimerization Versus Temperature in Various Methanol-Water Solutions

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APPENDIX A

DETERMINATION OF THE METHANOL CONTENT IN THE
METHANOL-WATER SOLUTIONS

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APPENDIX A

DETERMINATION OF THE METHANOL CONTENT IN THE
METHANOL-WATER SOLUTIONS

Methanol-water solutions were made up by pipetting appropriate volumes of methanol into a 100-ml volumetric flask. In order to determine the mass of methanol delivered from the pipettes, aliquots of methanol were transferred into 10-ml Erlenmeyer flasks where results of these experiments done in duplicate are listed below.

Table A-1. Mass of Methanol Delivered

| Pipette | MeOH mass | | Mean mass, and sample standard deviation | |
ml	gm	gm	gm	SD
1	13.06673	13.81173		
	12.28113	13.02735		
	0.78560	0.78338	0.7845 ±0.0016	
2	16.17825	14.71410		
	14.61249	13.15160		
	1.56276	1.55650	1.560 ±0.0044	
4	17.33276	16.51994		
	14.19039	13.36935		
	3.14237	3.15059	3.146 ±0.0058	
5	17.49474	17.55331		
	13.56523	13.61755		
	3.92951	3.93576	3.933 ±0.0044	
9	19.11314	20.50214		
	12.04081	13.43985		
	7.07223	7.06229	7.067 ±0.0071	
10	27.04200	25.07171		
	19.21609	17.22409		
	7.82591	7.84762	7.837 ±0.015	

The densities of the methanol-water solutions were determined by weighing 5-ml aliquots in a 10-ml Erlenmeyer flask. The volume delivered by the 5-ml pipette was determined by measuring the mass of water delivered at 25.2° C. The results of triplicate runs are shown below.

1.	17.95408	2.	17.70405	3.	17.67612
	12.97667		12.72245		12.70361
	4.97744 g		4.98160 g		4.97251 g

mean mass of water = 4.97718 ±0.0046 g

density of water at 25.2° C = 0.9970 g/ml

volume of pipette = 4.9922 ml

The determination of the density and volume of the methanol-water solutions are summarized below along with the identity of the pipettes used to make these solutions.

Table A-2. Density of Methanol-Water Solutions

Nominal Volume	Pipette	Volume of Solutions	Mass of 5-ml Aliquot	Density
ml		ml	g	g/ml
1	1	99.99	4.97485	0.9965
2	2	99.85	4.96193	0.9939
4	4	99.98	4.94865	0.9913
6	4 + 2	99.97	4.93301	0.9881
8	4 + 4	99.98	4.91459	0.9845
9	9	99.95	4.90222	0.9820
10	10	99.97	4.91079	0.9837
12	12 + 2	99.81	4.89381	0.9803
15	10 + 5	99.85	4.86768	0.9751
20	10 + 10	99.82	4.83549	0.9687

To test the precision in the preparation of the methanol-water solutions, duplicate solutions were made of the 1-, 4-, and 6-ml methanol solutions (triplicate solution was made of 4), and the densities determined as above. These results are summarized in table A-3. Determination A refers to the densities listed in the above table.

Table A-3. Precision of Density Measurements

MeOH Solution	Trial	Density, g/ml		
		A	B	C
ml				
1		0.9965	0.9967	---
4		0.9913	0.9911	---
6		0.9881	0.9879	0.9888

Based on these results, duplicate density measurements were not made on the solutions.

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APPENDIX B

ABSORBANCES AND DIMERIZATION CONSTANTS
OF CoTSPC IN METHANOL-WATER SOLUTIONS OF
VARIOUS TEMPERATURES

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Table B-1. Absorbances and Dimerization Constants Measured at 20.1° C

MeOH Solution	Absorbance, $\lambda = 662$ nm			Dimerization Constant, $M^{-1} \times 10^{-5}$		
	A	B	C	A	B	C
1	0.321	0.328	0.329	2.46	2.57	2.66
2	0.326	0.333	0.333	2.22	2.31	2.45
4	0.341	0.348	0.348	1.63	1.71	1.81
6	0.353	0.360	0.364	1.28	1.35	1.33
8	0.369	0.377	0.384	0.926	0.972	0.902
9	0.373	0.381	0.390	0.854	0.899	0.802
10	0.383	0.392	0.397	0.694	0.723	0.699
12	0.399	0.409	0.421	0.491	0.509	0.423
15	0.418	0.433	0.439	0.311	0.292	0.276
20	0.450	0.469	0.478	0.106	0.0836	0.0640

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Table B-2. Absorbances and Dimerization Constants Measured at 25.0° C

MeOH Solution	Absorbance, λ = 662 nm			Solution	Dimerization Constant, $M^{-1} \times 10^{-5}$		
	A	B	C		A	B	C
1	0.335	0.345	0.348		1.84	1.82	1.81
2	0.341	0.350	0.353		1.63	1.65	1.64
4	0.356	0.366	0.369		1.20	1.20	1.21
6	0.373	0.380	0.386		0.854	0.917	0.868
8	0.386	0.399	0.406		0.652	0.627	0.582
9	0.394	0.404	0.409		0.549	0.566	0.547
10	0.402	0.413	0.418		0.459	0.467	0.452
12	0.416	0.431	0.434		0.328	0.307	0.313
15	0.434	0.446	0.453		0.196	0.204	0.186
20	0.462	0.477	0.483		0.0510	0.0501	0.0442

Table B-3. Absorbances and Dimerization Constants Measured at 28.4° C

MeOH Solution	Absorbance, λ = 662 nm			Solution	Dimerization Constant, M^{-1} x 10^{-5}		
	A	B	C		A	B	C
1	0.348	0.359	0.361		1.41	1.38	1.41
2	0.355	0.366	0.368		1.23	1.20	1.23
4	0.371	0.380	0.384		0.889	0.917	0.902
6	0.388	0.392	0.403		0.625	0.723	0.619
8	0.399	0.415	0.419		0.491	0.447	0.442
9	0.406	0.418	0.422		0.418	0.418	0.414
10	0.414	0.426	0.427		0.345	0.347	0.369
12	0.426	0.440	0.444		0.250	0.242	0.242
15	0.445	0.457	0.460		0.132	0.141	0.147
20	0.467	0.483	0.484		0.0306	0.0273	0.0405

Table B-4. Absorbances and Dimerization Constants Measured at 34.4° C

MeOH Solution	Absorbance, λ = 662 nm			Dimerization Constant, M^{-1} x 10^{-4}		
	A	B	C	A	B	C
1	0.361	0.373	0.377	10.9	10.5	10.3
2	0.370	0.380	0.381	9.08	9.17	9.56
4	0.382	0.393	0.401	7.09	7.08	6.45
6	0.398	0.409	0.417	5.02	5.09	4.62
8	0.413	0.428	0.434	3.53	3.31	3.13
9	0.419	0.432	0.438	3.03	2.99	2.83
10	0.426	0.439	0.443	2.50	2.49	2.48
12	0.436	0.450	0.456	1.84	1.80	1.69
15	0.451	0.465	0.470	1.01	1.02	0.984
20	0.471	0.486	0.490	0.154	0.166	0.188

Table B-5. Absorbances and Dimerization Constants Measured at 40.5° C

MeOH Solution	Absorbance, λ = 662 nm			Solution	Dimerization Constants, $M^{-1} \times 10^{-4}$		
	A	B	C		A	B	C
1	0.378	0.393	0.394		7.70	7.08	7.42
2	0.388	0.401	0.403		6.25	6.02	6.19
4	0.400	0.411	0.416		4.80	4.87	4.72
6	0.412	0.424	0.432		3.62	3.64	3.28
8	0.427	0.442	0.449		2.43	2.29	2.10
9	0.433	0.445	0.450		2.03	2.10	2.04
10	0.438	0.453	0.457		1.72	1.63	1.63
12	0.446	0.460	0.465		1.27	1.26	1.22
15	0.459	0.473	0.479		0.639	0.664	0.599
20	0.475	0.490	0.494		0.0092	0.030	0.053

Table B-6. Absorbances and Dimerization Constants for Solution A Measured at 44.5° C

MeOH	Absorbance, $\lambda = 662$ nm	Dimerization Constant, $M^{-1} \times 10^{-4}$
1	0.389	6.12
2	0.398	5.02
4	0.408	3.99
6	0.420	2.95
8	0.435	1.90
9	0.439	1.66
10	0.444	1.37
12	0.451	1.01
15	0.462	0.510

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APPENDIX C

SLOPE OF PLOT OF ln(K) VERSUS ln(H$_2$O) FOR
CoTSPC, DIMERIZATION IN METHANOL-WATER SOLUTIONS

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Table C-1. Best-Fit Values of ln(K) From Fit of ln(K) Versus [H_2O] at Various Temperatures

[H_2O], M	15.7° C	20.1° C	25.0° C	28.4° C	34.4° C	40.5° C	44.5° C
55.55	12.972	12.729	12.395	12.147	11.893	11.745	11.182
54.92	12.812	12.549	12.206	11.952	11.685	11.489	11.003
54.27	12.638	12.353	11.999	11.739	11.458	11.211	10.89
53.31	12.377	12.058	11.689	11.420	11.118	10.793	10.514
52.26	12.087	11.730	11.345	11.066	10.740	10.329	10.185
51.19	11.797	11.403	11.001	10.711	10.362	9.865	9.858
50.60	11.523	11.207	10.795	10.499	10.135	9.586	9.662
50.28	11.536	11.108	10.691	10.392	10.022	9.447	9.564
49.13	11.188	10.715	10.278	9.967	9.568	8.890	9.171
47.55	10.724	10.191	9.727	9.400	8.964	8.147	8.648
44.94	9.897	9.258	8.746	8.390	7.886	6.824	--

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APPENDIX D

RESULTS OF APPLYING BLANDAMER'S METHOD TO
VARIOUS METHANOL-WATER SOLUTIONS

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Appendix D

Table D-1. Application of Blandamer's Method - 8.89 Mole Percent MeOH

T	K	K fit	$-\Delta H^\circ$	ΔC_p°
°C	$M^{-1} \times 10^{-5}$	$M^{-1} \times 10^{-5}$	kcal/mole	cal/mole-K
15.7	3.12	3.13	12.6 ±0.6	74 ±64[a]
20.1	2.33	2.29	13.4 ±0.8	157 ±89
25.0	1.64	1.64	12.4 ±0.5	98 ±82
28.4	1.22	1.31	12.5 ±0.5	309 ±100
34.4	0.927	0.888	10.8 ±0.9	84 ±139
40.5	0.615	0.608	10.5 ±0.8	136 ±87
44.5	0.502	0.478	10.0 ±0.8	132 ±66

[a] Error is standard deviation of the mean.

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Table D-2. Application of Blandaner's Method - 1.81 Mole Percent MeOH

T	K	K fit	$-\Delta H°$	$\Delta C_p°$
°C	$M^{-1} \times 10^{-5}$	$M^{-1} \times 10^{-5}$	kcal/mole	cal/mole-K
15.7	2.34	2.33	13.4 ±0.5[a]	159 ±52[a]
20.1	1.72	1.71	13.8 ±0.6	241 ±73
25.0	1.20	1.22	12.4 ±0.4	192 ±67
28.4	0.903	0.974	12.1 ±0.4	370 ±81
34.4	0.686	0.661	10.2 ±0.7	173 ±112
40.5	0.480	0.453	9.0 ±0.7	232 ±72
44.5	0.399	0.356	8.4 ±0.6	214 ±56

[a]Error is standard deviation of the mean.

Table D-3. Applications of Blandamer's Method - 2.74 Mole Percent MeOH

T	K	K fit	$-\Delta H°$	$\Delta C_p°$
°C	$M^{-1} \times 10^{-5}$	$M^{-1} \times 10^{-5}$	kcal/mole	cal/mole-K
15.7	1.78	1.78	14.4 ±0.5[a]	214 ±50[a]
20.1	1.32	1.29	15.6 ±0.6	371 ±67
25.0	0.880	0.908	13.6 ±0.4	345 ±57
28.4	0.656	0.718	12.8 ±0.4	483 ±73
34.4	0.491	0.480	10.1 ±0.7	300 ±106
40.5	0.351	0.323	8.1 ±0.7	362 ±69
44.5	0.295	0.252	7.2 ±0.7	332 ±55

[a]Error is standard deviation of the mean.

Table D-4. Application of Blandamer's Method - 3.69 Mole Percent MeOH

T	K	K fit	$-\Delta H^\circ$	ΔC_p°
°C	$M^{-1} \times 10^{-5}$	$M^{-1} \times 10^{-5}$	kcal/mole	cal/mole-K
15.7	1.40	1.38	16.4 ±0.4[a]	278 ±41[a]
20.1	0.933	0.955	15.6 ±0.5	302 ±59
25.0	0.620	0.644	13.9 ±0.3	263 ±52
28.4	0.460	0.494	13.3 ±0.3	401 ±66
34.4	0.332	0.313	11.0 ±0.6	254 ±95
40.5	0.227	0.201	9.7 ±0.6	287 ±57
44.5	0.190	0.141	8.5 ±0.5	288 ±43

[a]Error is standard deviation of the mean.

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Table D-5. Application of Blandamer's Method - 4.18 Mole Percent MeOH

T	K	K fit	$-\Delta H°$	$\Delta C_p°$
°C	$M^{-1} \times 10^{-5}$	$M^{-1} \times 10^{-5}$	kcal/mole	cal/mole-K
15.7	12.4	12.3	16.1 ±0.3[a]	252 ±30[a]
20.1	8.52	8.55	16.1 ±0.4	328 ±47
25.0	5.54	5.78	14.4 ±0.2	323 ±38
28.4	4.17	4.45	13.5 ±0.2	389 ±48
34.4	2.95	2.83	11.2 ±0.6	281 ±83
40.5	2.06	1.82	9.3 ±0.5	333 ±47
44.5	1.66	1.29	8.8 ±0.5	285 ±38

[a]Error is standard deviation of the mean.

Table D-6. Application of Blandamer's Method - 4.65 Mole Percent MeOH

T	K	K fit	$-\Delta H^\circ$	ΔC_p°
°C	$M^{-1} \times 10^{-4}$	$M^{-1} \times 10^{-4}$	kcal/mole	cal/mole-K
15.7	10.0	9.94	15.2 ±0.3[a]	191 ±27[a]
20.1	7.05	7.00	15.6 ±0.4	275 ±50
25.0	4.59	4.79	14.3 ±0.3	305 ±45
28.4	3.54	3.71	13.3 ±0.2	296 ±41
34.4	2.49	2.40	11.4 ±0.7	217 ±97
40.5	1.66	1.56	10.4 ±0.5	242 ±51
44.5	1.37	1.12	9.4 ±0.4	243 ±38

[a]Error is standard deviation of the mean.

Table D-7. Application of Blandamer's Method - 5.63 Mole Percent MeOH

T	K	K fit	$-\Delta H°$	$\Delta C_p°$
°C	$M^{-1} \times 10^{-4}$	$M^{-1} \times 10^{-4}$	kcal/mole	cal/mole-K
15.7	7.50	7.27	17.4 ±0.4[a]	357 ±43[a]
20.1	4.74	5.02	14.8 ±0.5	283 ±52
25.0	3.16	3.36	13.5 ±0.3	303 ±45
28.4	2.45	2.56	12.6 ±0.2	328 ±46
34.4	1.78	1.61	10.6 ±0.6	223 ±96
40.5	1.25	1.03	8.9 ±0.5	289 ±51
44.5	1.01	0.718	8.7 ±0.5	241 ±44

[a]Error is standard deviation of the mean.

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Table D-8.   Application of Blandamer's Method - 7.17 Mole Percent MeOH

T	K	K fit	$-\Delta H^\circ$	ΔC_p°
°C	$M^{-1} \times 10^{-4}$	$M^{-1} \times 10^{-4}$	kcal/mole	cal/mole-K
15.7	4.73	4.63	17.8 ±0.6[a]	273 ±60[a]
20.1	2.93	3.08	15.5 ±0.7	198 ±88
25.0	1.95	1.99	14.3 ±0.5	130 ±81
28.4	1.40	1.48	14.3 ±0.5	345 ±101
34.4	1.00	0.89	12.3 ±0.9	158 ±135
40.5	0.634	0.54	11.8 ±0.8	182 ±81
44.5	0.51	0.37	10.9 ±0.7	191 ±61

[a]Error is standard deviation of the mean.

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Table D-9. Application of Blandamer's Method - 9.81 Mole Percent MeOH

T	K	K fit	$-\Delta H^\circ$	ΔC_p°
°C	$M^{-1} \times 10^{-4}$	$M^{-1} \times 10^{-4}$	kcal/mole	cal/mole-K
15.7	1.79	1.76	25.6 ±0.3[a]	372 ±44[a]
20.1	0.845	0.926	19.4 ±0.4	-120 ±84
25.0	0.487	0.463	20.0 ±0.3	-146 ±114
28.4	0.328	0.290	20.3 ±0.8	-60 ±199
34.4	0.169	0.130	26.6 ±0.8	-48 ±165

[a]Error is standard deviation of the mean.

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APPENDIX E

THERMODYNAMIC PARAMETERS FOR THE
DIMERIZATION OF CoTSPC IN METHANOL-WATER

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Table E-1. Temperature Fit of 0.0089 Mole Fraction Methanol

T °C	K $M^{-1} \times 10^{-5}$	$-\Delta F^\circ$ kcal/mole	$-\Delta F^\circ$ fit kcal/mole	K fit $M^{-1} \times 10^{-5}$	$-\Delta H^\circ$ kcal/mole	$-\Delta S^\circ$ cal/mole	$-\Delta C_p^\circ$ cal/mole-K	$-T\Delta S^\circ$ kcal/mole
15.7	3.12	7.26	7.27	3.15	12.6	18.3	64	5.3
30.1	2.33	7.20	7.19	2.28	12.3	17.3	65	5.1
25.0	1.64	7.11	7.11	1.62	12.0	16.2	66	4.8
28.4	1.22	7.02	7.05	1.29	11.7	15.5	67	4.7
34.4	0.927	6.99	6.96	0.888	11.3	14.2	68	4.4
40.5	0.615	6.87	6.88	0.625	10.9	12.8	69	4.0
44.5	0.502	6.83	6.83	0.502	10.6	11.9	70	3.8

A = -21.783 ±1010

B = 82.2 ±67

C = -0.1106 ±0.11

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Table E-2. Temperature Fit of 0.0181 Mole Fraction Methanol

T	K	$-\Delta F^\circ$	$-\Delta F^\circ$ fit	K fit	$-\Delta H^\circ$	$-\Delta S^\circ$	$-\Delta C^\circ_p$	$-T\Delta S^\circ$
°C	$M^{-1} \times 10^{-5}$	kcal/mole	kcal/mole	$M^{-1} \times 10^{-5}$	kcal/mole	cal/mole	cal/mole-K	kcal/mole
15.7	2.34	7.10	7.10	2.36	13.4	21.7	147	6.3
20.1	1.72	7.02	7.10	1.68	12.7	19.4	149	5.7
25.0	1.20	6.93	6.92	1.19	12.0	16.9	151	5.0
28.4	0.903	6.84	6.87	0.950	11.5	15.2	153	4.6
34.4	0.686	6.81	6.78	0.664	10.5	12.2	156	3.7
40.5	0.480	6.72	6.72	0.482	9.6	9.1	159	2.8
44.5	0.399	6.69	6.69	0.400	8.9	7.0	161	2.2

A = -34,550 ±8518
B = 168.4 ±56
C = 0.2540 ±0.09

Table E-3. Temperature Fit of 0.0274 Mole Fraction Methanol

T °C	K $M^{-1} \times 10^{-5}$	$-\Delta F°$ kcal/mole	$-\Delta F°$ fit kcal/mole	K fit $M^{-1} \times 10^{-5}$	$-\Delta H°$ kcal/mole	$-\Delta S°$ cal/mole	$-\Delta C_p°$ cal/mole-K	$-T\Delta S°$ kcal/mole
15.7	1.78	6.94	6.95	1.82	14.6	26.3	210	7.6
20.1	1.32	6.87	6.84	1.26	13.6	23.1	214	6.8
25.0	0.880	6.74	6.74	0.871	12.6	19.6	217	5.8
28.4	0.656	6.65	6.68	0.691	11.8	17.1	220	5.2
34.4	0.491	6.60	6.59	0.480	10.5	12.7	224	3.9
40.5	0.351	6.52	6.52	0.352	9.1	8.3	229	2.6
44.5	0.295	6.50	6.50	0.295	8.2	5.3	231	1.7

A = -44,959 ±9.775

B = 23.8 ±64

C = 0.3644 ±0.11

Table E-4. Temperature Fit of 0.0369 Mole Fraction Methanol

T	K	-ΔF°	-ΔF° fit	K fit	ΔH°	-ΔS°	-ΔCp°	-TΔS°
°C	M⁻¹ x 10⁻⁵	kcal/mole	kcal/mole	M⁻¹ x 10⁻⁵	kcal/mole	cal/mole	cal/mole-K	kcal/mole
15.7	1.40	6.80	6.80	1.40	16.3	32.3	253	9.5
20.1	0.933	6.67	6.67	0.928	15.2	28.9	257	8.5
25.0	0.620	6.53	6.53	0.616	13.9	24.6	261	7.3
28.4	0.460	6.43	6.46	0.477	13.0	21.7	264	6.5
34.4	0.332	6.36	6.34	0.321	11.4	16.4	269	5.1
40.5	0.227	6.25	6.26	0.229	9.7	11.1	274	3.5
44.5	0.190	6.22	6.22	0.190	8.6	7.6	278	2.4

$A = -52,769 \pm 6724$

$B = 285.5 \pm 44$

$C = -0.4375 \pm 0.07$

Table E-5. Temperature Fit of 0.0418 Mole Fraction Methanol

T	K	$-\Delta F°$	$-\Delta F°$ fit	K fit	$-\Delta H°$	$-\Delta S°$	$-\Delta C_p°$	$-T\Delta S°$
°C	$M^{-1} \times 10^{-4}$	kcal/mole	kcal/mole	$M^{-1} \times 10^{-4}$	kcal/moie	cal/mole	cal/mole-K	kcal/mole
15.7	12.4	6.73	6.74	12.5	15.9	31.7	221	9.2
20.1	8.52	6.62	6.60	8.34	14.9	28.3	224	8.3
25.0	5.54	6.47	6.47	5.56	13.8	24.6	228	7.3
28.4	4.17	6.37	6.39	4.31	13.0	22.0	231	6.6
34.4	2.95	6.29	6.28	2.89	11.6	17.4	235	5.3
40.5	2.06	6.19	6.18	2.04	10.2	12.7	240	4.0
44.5	1.66	6.13	6.14	1.68	9.2	9.6	243	3.1

A = -47,807 ±6170

B = 252.7 ±41

C = -0.3826 ±0.07

Table E-6. Temperature Fit of 0.0465 Mole Fraction Methanol

T	K	-ΔF°	-ΔF° fit	K fit	-ΔH°	-ΔS°	-ΔC$_p$°	-TΔS°
°C	M^{-1} x 10^{-4}	kcal/mole	kcal/mole	M^{-1} x 10^{-4}	kcal/mole	cal/mole	cal/mole-K	kcal/mole
15.7	10.0	6.61	6.61	10.1	15.0	29.1	163	8.4
20.1	7.05	6.50	6.49	6.88	14.3	26.6	164	7.8
25.0	4.59	6.36	6.37	4.65	13.5	23.8	168	7.1
28.4	3.54	6.28	6.29	3.62	12.9	21.9	170	6.6
34.4	2.49	6.19	6.17	2.42	11.9	18.5	173	5.7
40.5	1.66	6.06	6.07	1.69	10.8	15.1	177	4.7
44.5	1.37	6.01	6.01	1.36	10.1	12.8	179	4.1

A = -38,541 ±6376

B = 192.0 ±42

C = -0.2820 ±0.07

Table E-7. Temperature Fit of 0.0563 Mole Fraction Methanol

T	K	-ΔF°	-ΔF° fit	K fit	-ΔH°	-ΔS°	-ΔC_p°	-TΔS°
°C	M^{-1} x 10^{-4}	kcal/mole	kcal/mole	M^{-1} x 10^{-4}	kcal/mole	cal/mole	cal/mole-K	kcal/mole
15.7	7.50	6.44	6.43	7.31	16.3	34.2	274	9.9
20.1	4.74	6.27	6.29	4.84	15.1	30.1	278	8.8
25.0	3.16	6.14	6.15	3.22	13.7	25.4	283	7.6
28.4	2.45	6.06	6.07	2.51	12.8	22.2	286	6.7
34.4	1.78	5.98	5.95	1.70	11.0	16.5	292	5.1
40.5	1.25	5.88	5.87	1.23	9.2	10.7	298	3.4
44.5	1.01	5.82	5.83	1.03	8.0	6.9	302	2.2

A = -55.936 ±9108

B = 308.5 ±60

C = 0.4747 ±0.1

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Table E-8. Temperature Fit of 0.0717 Mole Fraction Methanol

T	K	-ΔF°	-ΔF° fit	K fit	-ΔH°	-ΔS°	-ΔC°$_p$	-TΔS°
°C	M⁻¹ × 10⁻⁴	kcal/mole	kcal/mole	M⁻¹ × 10⁻⁴	kcal/mole	cal/mole	cal/mole-K	kcal/mole
15.7	4.73	6.18	6.17	4.63	17.1	37.8	221	10.9
20.1	2.93	5.99	6.01	3.00	16.1	34.5	224	10.1
25.0	1.95	5.85	5.85	1.93	15.0	30.7	228	9.2
28.4	1.40	5.72	5.75	1.46	14.02	28.7	230	8.5
34.4	1.00	5.63	5.59	0.942	12.8	23.5	235	7.2
40.5	0.634	5.46	5.46	0.641	11.4	18.9	240	5.9
44.5	0.51	5.39	5.39	0.51	10.4	15.8	243	5.0

A = -48.977 ±1.067

B = 258.6 ±70

C = -0.3821 ±0.11

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Table E-9. Temperature Fit of 0.0981 Mole Fraction Methanol

T	K	-ΔF°	-ΔF° fit	K fit	-ΔH°	-ΔS°	-ΔC°p	-TΔS°
°C	M^{-1} x 10^{-4}	kcal/mole	kcal/mole	M^{-1} x 10^{-4}	kcal/mole	cal/mole	cal/mole-K	kcal/mole
15.7	1.79	5.62	5.60	1.73	25.7	69.7	418	20.1
20.1	0.845	5.27	5.31	0.906	23.9	63.4	424	18.6
25.0	0.487	5.03	5.02	0.476	21.8	56.3	432	16.8
28.4	0.328	4.85	4.83	0.319	23.3	51.3	436	15.5
34.4	0.169	4.54	4.55	0.172	17.7	42.7	445	13.1

A = -86,125 ±4,035

B = 487.8 ±271

C = -0.7237 ±0.45

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